Synthetic Studies of Substituted 2,3-Naphthalocyaninatozinc(II) Complexes

By

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Abbreviations

DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DMF	*N, N*-Dimethylformamide
DMSO	Dimethylsulfoxide
DSC	Differential scanning calorimetry
dppp	1,3-Bis(diphenylphosphino)propane
EI	Electron impact
equiv.	Equivalent
FAB	Fast atom bombardment
FT	Fourier transform
HMPA	Hexamethylphosphoric triamide
HOMO	Highest occupied molecular orbital
ICR	Ion cyclotron resonance
IR	Infrared
LB	Langmuir-Blodgett
LSI	Liquid secondary-ion
LUMO	Lowest unoccupied molecular orbital
MS	Mass spectrometry
NBS	*N*-Bromosuccinimide
Nc	2,3-Naphthalocyanine
NMR	Nuclear magnetic resonance
OAc	Acetate
Pc	Phthalocyanine
THF	Tetrahydrofuran
UV-Vis	Ultraviolet-visible
vt	Virtual triplet

Abstract

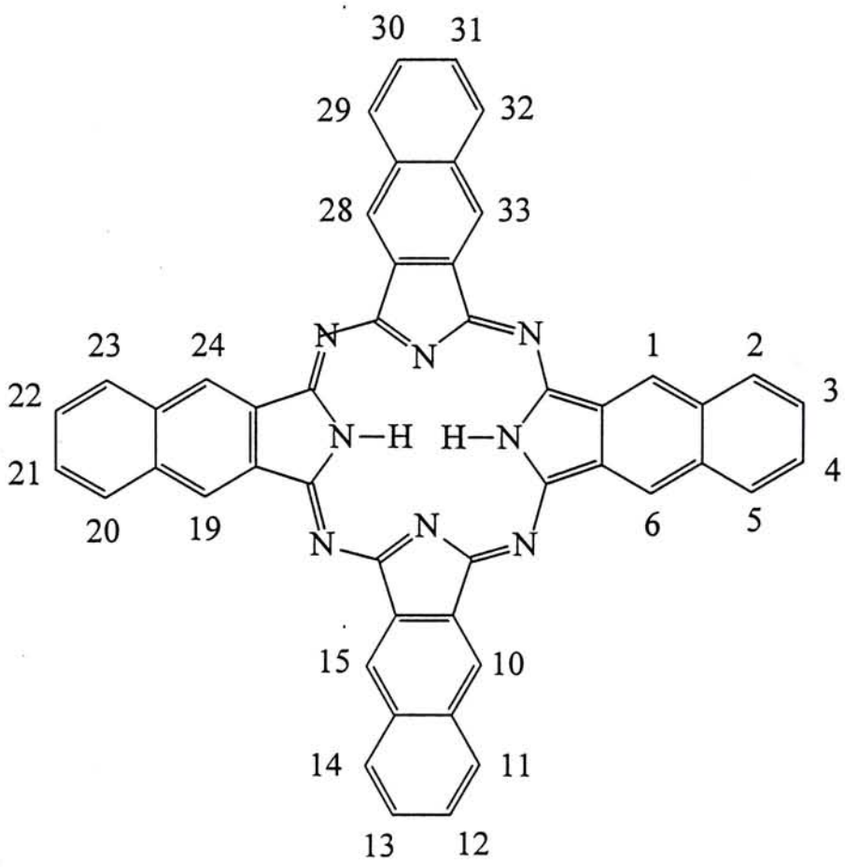
This thesis describes the synthesis and spectroscopic properties of a series of octa- and hexadeca-substituted 2,3-naphthalocyaninato zinc complexes. Two general routes to differently substituted 2,3-dicyanonaphthalenes have been developed which can be cyclized in the presence of $Zn(OAc)_2 \cdot 2H_2O$ and DBU to the corresponding naphthalocyanines. The aggregation behavior of these macrocycles have been investigated by ^1H NMR and UV-Vis spectroscopy. The effects of substituents on their absorption spectra are also discussed.

Long-chain substituents can also be incorporated onto the peripheral of 2,3-naphthalocyanine by using similar pathways. The resulting marcocycles show a lower tendency to form molecular aggregates and exhibit liquid crystalline properties. To our knowledge, these represent the first discotic mesogens based on 2,3-naphthalocyanine core. The synthesis, spectroscopy and liquid crystalline properties of these novel marcocyclic compounds are presented in the latter part of this thesis.

1. Introduction

Phthalocyanine (Pc) was synthesized accidentally in 1907.[1] Over the past few decades, this macrocyclic compound and its analogs have been extensively studied.[2] Pcs are among the most stable organic materials showing remarkable optical properties. The conjugated macrocycles which contain 42 π electrons, absorb strongly in the far red end of the visible region (*ca.* 670 nm, Q band) and in the near-ultraviolet region (*ca.* 340 nm, B or Soret band). The intense color and high thermal and chemical stability of these compounds account for their usage as dyes and pigments for long time. Pcs are also of great interest owing to their novel electrical properties.[3] They are well-known as good photoconductors and are, at present, used in electrophotographic systems[4] and photovoltaic cells for energy conversion.[5] They can also form highly conducting materials. The packing of phthalocyanine molecules in columnar stacks leads to an effective overlap between the π molecular orbitals of adjacent macrocycles, which provides an electronic pathway for delocalization of the charge carriers generated upon oxidation. Cocrystallization of Pcs with oxidizing agents like iodine yields 'molecular metals' with conductivities in the range of 10-1000 S cm^{-1} at room temperature.[6] Pcs are thus excellent candidates for molecular electronic materials. Indeed, they have already been widely used in highly sensitive gas sensors,[7] rectifier (molecular diodes),[8] and transistors.[9] The applications of Pcs in many other areas such as optical data storage,[10] nonlinear optics,[11] electrochromic devices,[12] liquid crystals,[13] Langmuir-Blodgett (LB) films,[14] and photosensitizers in photodynamic therapy[15] have also been documented.

2,3-Naphthalocyanine Nc (**1**), is a Pc's analog which has annulated benzene rings and consists of 54 π electrons. Similar to Pcs, this class of extended macrocycles is very thermally and chemically stable, and is only sensitive towards redox reactions. However, linear benzoannulation strongly affects the electronic properties of the macrocycles. It produces a destabilization of the HOMO leading to lower ionization energies and oxidation potentials. In addition, it reduces the HOMO-LOMO energy gap, thus shifting the intense Q band absorption to the near-IR region (*ca.* 800 nm). This bathochromic shift makes Ncs excellent candidates for high-density optical recording (ODR) media since long-wavelength absorbing dyes are required in the writing and reading processes using semiconductor lasers.[16]

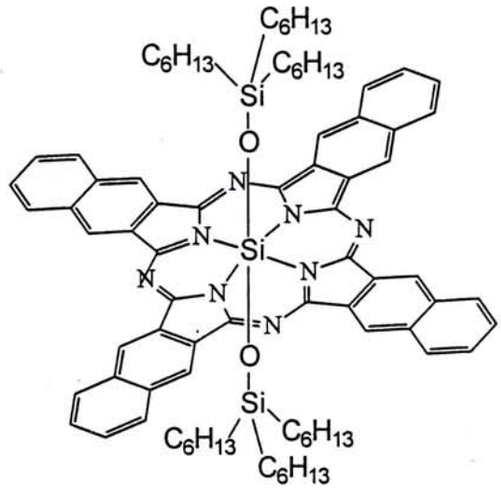


Metal-free 2,3-Naphthalocyanine (1)

In recent years, photodynamic therapy of tumors has received considerable attention from the biomedical community. Upon photolysis, photosensitizers are excited to the triplet state which transfers energy to the molecular oxygen giving the energetic singlet oxygen ($^1\Delta g$) species. It is generally believed that this species is responsible for the initial state of tissue damage. As radiation with longer wavelength (600-1200 nm) penetrates deeper into tissues, the search for effective photodynamic sensitizers with high extinction coefficients in the deep red region has been undertaken. For efficient energy transfer, the triplet energy levels of such sensitizers should be close to the energy level of singlet oxygen (22.5 Kcal / mol).[17] Rodgers *et al.* showed that the triplet (T1) energy of bis(tri-*n*-hexylsiloxy)silicon 2,3-naphthalocyanine (SiNc) (**2**) is 1.0 Kcal / mol lower than that of singlet molecular oxygen (22.5 Kcal / mol) and the energy transfer from the triplet state of SiNc to O_2 to produce singlet oxygen is a reversible reaction. The efficiency of conversion of the triplets into singlet oxygen is near 100% because the SiNc triplet is intrinsically long-lived.

Although Ncs are useful materials, unsubstituted Nc is almost insoluble in most of the common organic solvents. It can only be dissolved slightly in high boiling solvents such as 1-chloronaphthalene, quinoline, and HMPA etc.. Because of this, spectroscopic data were mainly obtained in solid states such as single crystals, powder, and thin films. The poor solubility may derive in large part from the strong molecular aggregation arising from the π-π interactions among the marcocycles. As the π-system of Ncs is larger than that of Pcs, the aggregation tendency of Ncs is even greater and the interactions are more difficult to be disrupted. In order to solve this problem, flexible and bulky side chains can be introduced to the compounds so that the distance between

two Nc molecules is increased and the degree of aggregation is thus reduced. In general, substituents can be introduced as the axial ligands or to the peripheral of the macrocycle. The former case has been well-documented for group (IV) and late transition metal complexes.[18,19] For example, Kenney *et al.* have synthesized a bisaxial coordinated silicon naphthalocyanine, namely bis(tri-*n*-hexylsiloxy)naphthalocyaninatosilicon(IV) [$SiNc(OC_6H_{13})_2$] (**2**). The two bulky siloxyether ligands prevent the stacking of two Nc molecules and this compound can thus be dissolved in a wide range of solvents such as benzene, dichloromethane, and other halogenated solvents.[20] Hayashi *et al.* have also synthesized a series of related silicon naphthalocyanines, [$SiNc(OR)_2$, R = C_2H_5, *n*-C_3H_7, and *n*-C_4H_9].[21] Germanium naphthalocyanines $GeNc[(OSiR_3)]_2$ (R = C_2H_5, and C_4H_9) have been reported by Iwakabe *et al.* recently.[22] Apart from these silicon and germanium Ncs, iron(II) and Ru(II) Ncs coordinated with axial ligands have also been reported.[23,24] They are either coordinated with donor ligands [$MNc(R)_8L_2$] (R = OC_6H_{13}; M = Fe, Ru; L = ^{t}BuNC, pyridine) or polymeric $[MNcL]_n$ (M = Fe, Ru; L = dicyanoacetylene, s-tetrazine).[25] They are all soluble in common organic solvents and can be characterized by NMR and UV-Vis spectroscopy. It is worth noting that although the solubility of these axially substituted Ncs is increased, the introduction of axial ligands does not significantly affect the position of the Q band absorption (shift 3-7 nm usually).[20-24]



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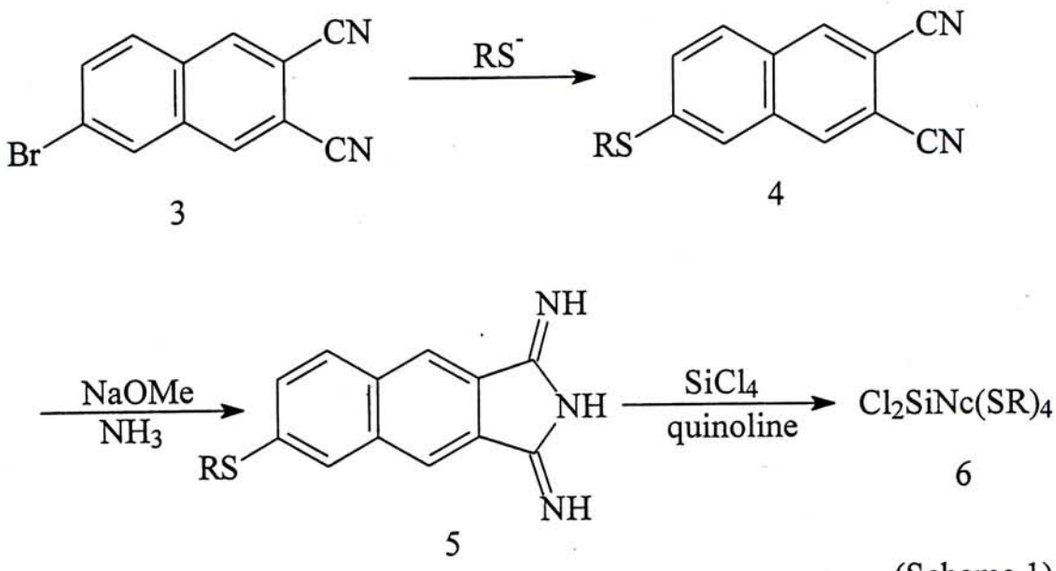
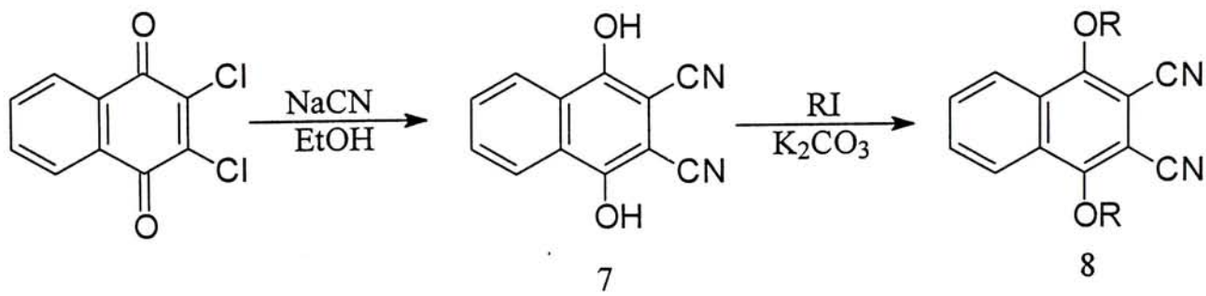
Substitution on the periphery of the Nc ring system can also enhance the solubility of Ncs in organic solvents. However, substituted Ncs were relatively rare when we initiated this project which is probably due to the shortage of convenient synthetic route to the precursors substituted 2,3-dicyanonaphthalenes. Most of the known Ncs are either tetrasubstituted or octasubstituted. The former Ncs contain only one substituent in each of the naphthalene ring and therefore exist as a mixture of four structural isomers which are extremely difficult to be separated. The latter Ncs are symmetrical compounds. The substituents can be located at either (1,6,10,15,19,24,28,33), (2,5,11,14,20,23,29,32) or (3,4,12,13,21,22,30,31) positions of the Nc ring.

A series of highly soluble Ncs $Cl_2SiNc(SR)_4$ **6** (R = butyl, hexyl, decyl, and hexadecyl) which have four ring substituents have been reported by Hayashi *et al.*[26] as shown in Scheme 1. Cross-coupling reactions of 6-bromo-2,3-dicyanonaphthalene (**3**) with alkylthiolate ions give the corresponding aryl sulfide **4,** which are then converted to $Cl_2SiNc(SR)_4$ **6** through the bisisoindolines **5**.

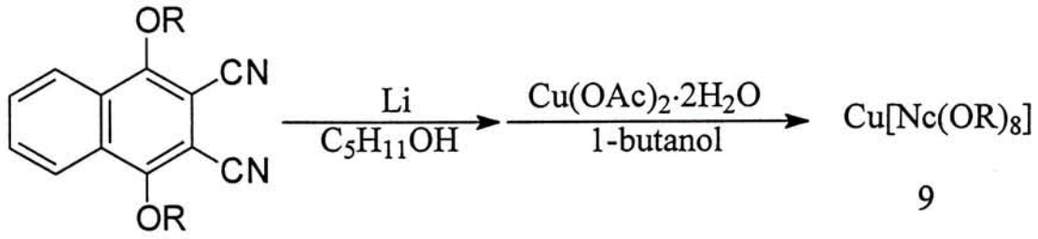


(Scheme 1)

1,4-Dialkyloxy-2,3-dicyanonaphthalenes (**8**) (R = ethyl, propyl, butyl, pentyl or octyl) have been prepared by *O*-alkylation of the diol **7** with appropriate alkyl iodide (Scheme 2). Diol **7** can be obtained by treating 2,3-dichloro-1,4-naphthoquinone with sodium cyanides.[26] Dinitriles **8** have been converted to the respective metal-free naphthalocyanines in 10-30% yield by utilizing either lithium metal in pentanol or butyllithium in THF, followed by protonation. The naphthalocyaninatocopper(II) complexes **9** have also been prepared from the corresponding metal-free naphthalocyanines and copper(II) acetate in refluxing 1-butanol (Scheme 3).[27]



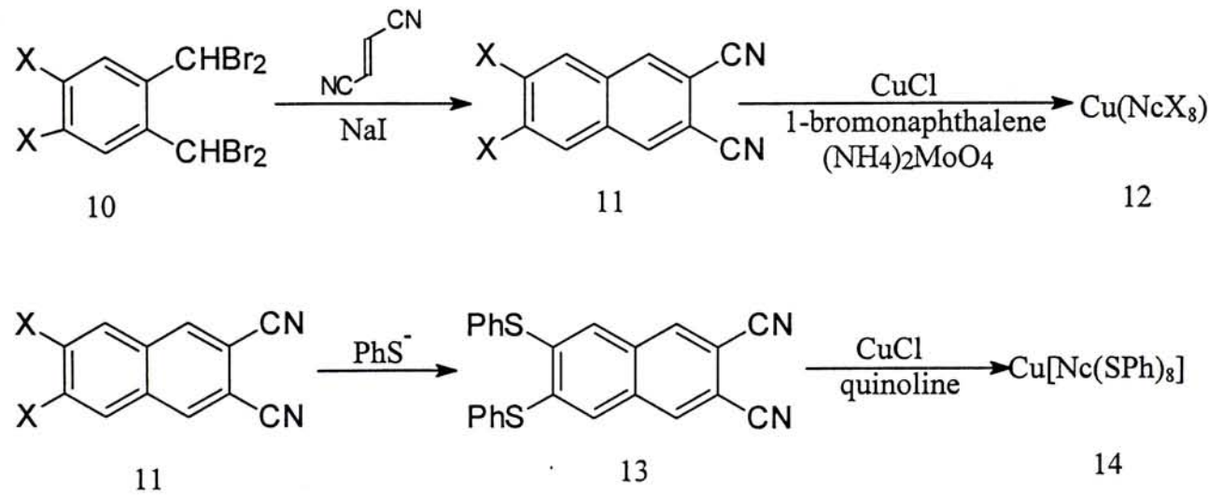
(Scheme 2)



9

8 R = ethyl, propyl, butyl, pentyl, or octyl (Scheme 3)

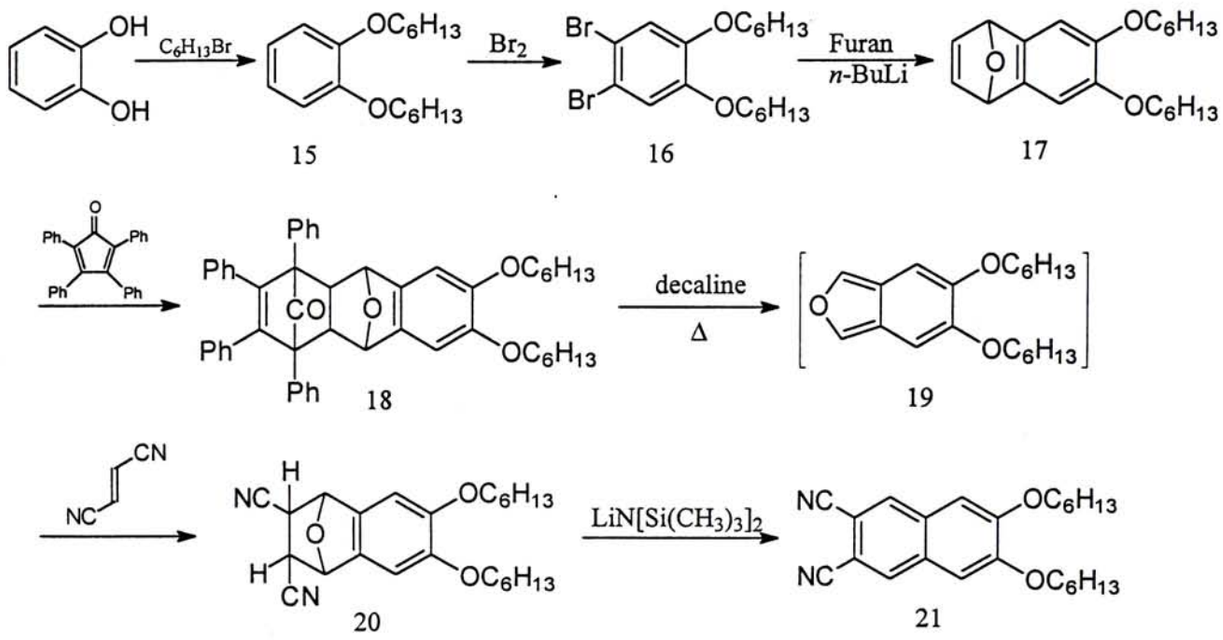
Halogenated 2,3-dicyanonaphthalenes **11** (X = Br or Cl) have been prepared by condensation of halogenated 1,2-bis(dibromomethyl)benzenes **10** (X = Br or Cl) with fumaronitrile in DMF in the presence of sodium iodide (Scheme 4).[28] The octahalogenated naphthalocyaninatocopper(II) complexes **12** (X = Br or Cl) can be synthesized by fusing **11** in the presence of copper(I) chloride and a catalytic amount of ammonium molybdate in 1-bromonaphthalene.[29] Treatment of **11** with thiophenolate gave **13** in 20% yield, which can be cyclized with CuCl, in quinoline to give **14**.[30] The solubility of these compounds are very poor and so they have only been characterized with IR and elemental analyses.



(Scheme 4)

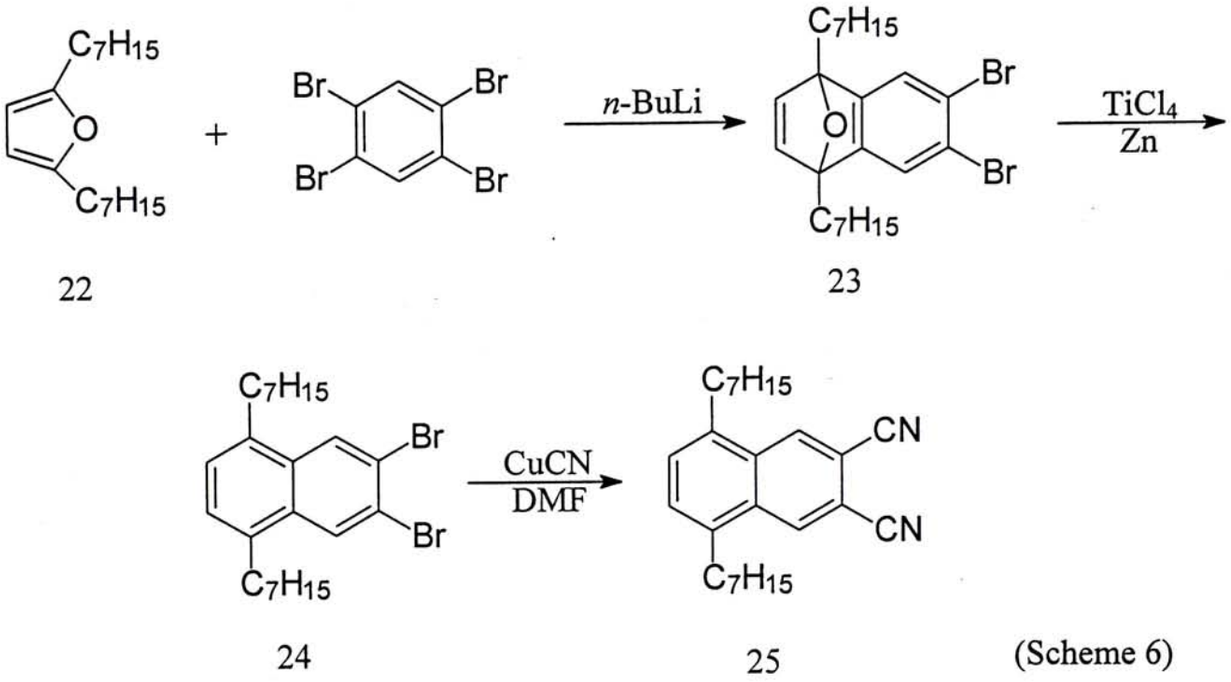
During the course of this work, Hanack *et al.* have reported the syntheses of 2,3-dicyano-6,7-dihexyloxynaphthalene (**21**) and 2,3-dicyano-5,8-diheptylnaphthalene (**25**)

have been reported.[24] The dinitrile **21** has been prepared from catechol by the route shown in Scheme 5. Catechol can be converted into the ether **15** by standard *O*-alkylation which undergoes bromination to yield the dibromide **16**. Treatment of **16** with n-butyllithium and furan gives the epoxide **17**. In a second Diels-Alder reaction, **17** reacts with tetraphenylcyclopentadienone affording the adduct **18**. In boiling decaline, **18** decomposes giving the intermediate dihexyoxyisobenzofuran (**19**), which can be trapped with fumaronitrile to give the tetrahydronaphthalene **20**. The dinitrile **21** is formed from **20** by dehydration using lithium bis(trimethylsilyl)amide as a base.



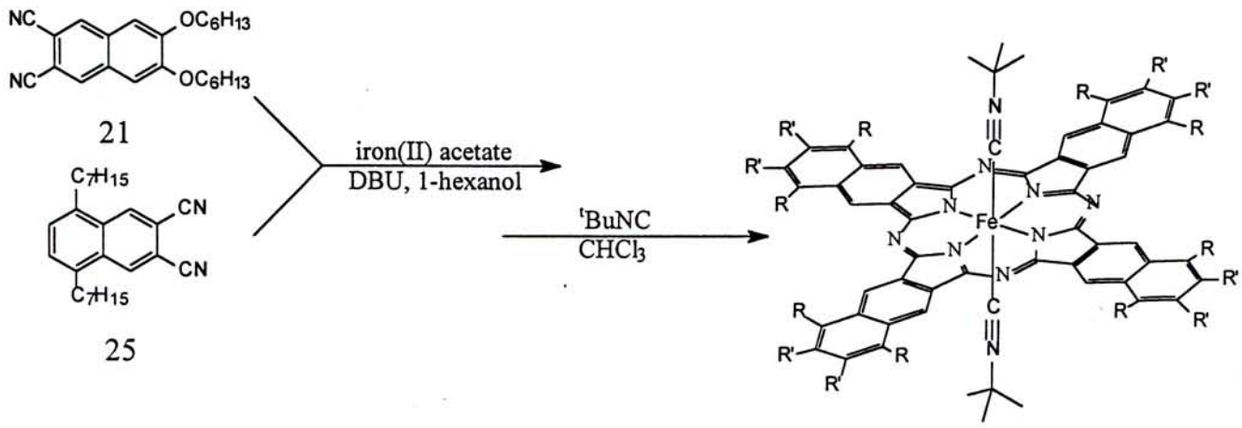
(Scheme 5)

2,3-Dicyano-5,8-diheptylnaphthalene (**25**) has been synthesized by the reaction pathway shown in Scheme 6. Treatment of 1,2,4,5-tetrabromobenzene with 1 equiv. of butyllithium gives a benzyne intermediate which is trapped with 2,5-diheptylfuran (**22**)[31] to give the adduct **23**. Reductive deoxygenation of **23** with zinc / titanium tetrachloride[32] gives **24**, which undergoes the Rosenmund-von Braun reaction giving the dinitrile **25**.



22 23 24 25 (Scheme 6)

The dinitriles **21** and **25** upon treatment with iron(II) acetate and DBU in 1-hexanol, followed by the addition of tert-butylisocyanide, are converted to the naphthalocyaninatoiron(II) complexes **26** and **27**, respectively (Scheme 7).[24] Due to the bulky axial tert-butylisocyano ligands, these compounds do not show aggregation.

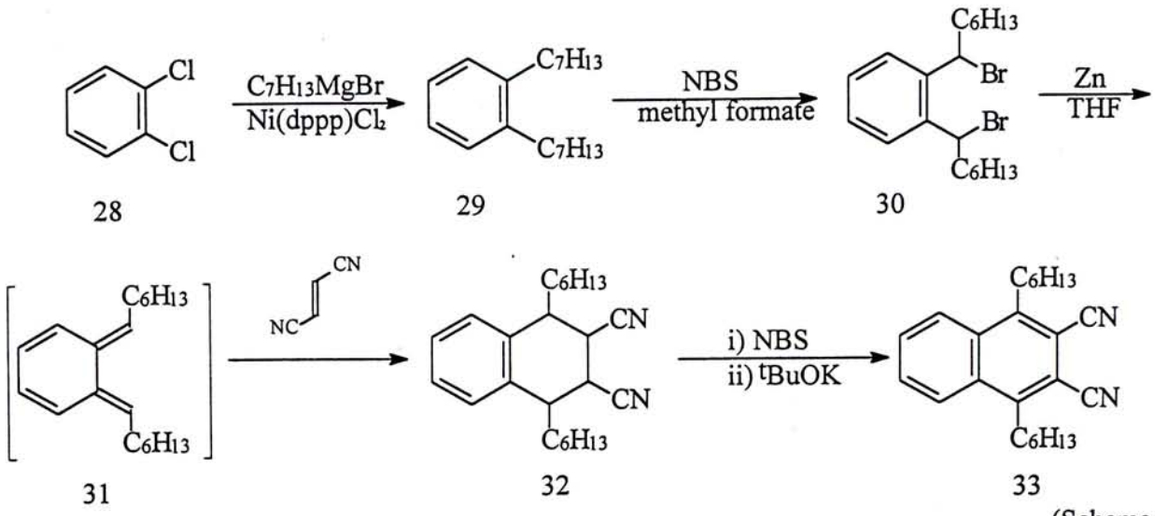


26 R = H R' = OC_6H_{13}

27 R = *n*-C_7H_{15} R' = H

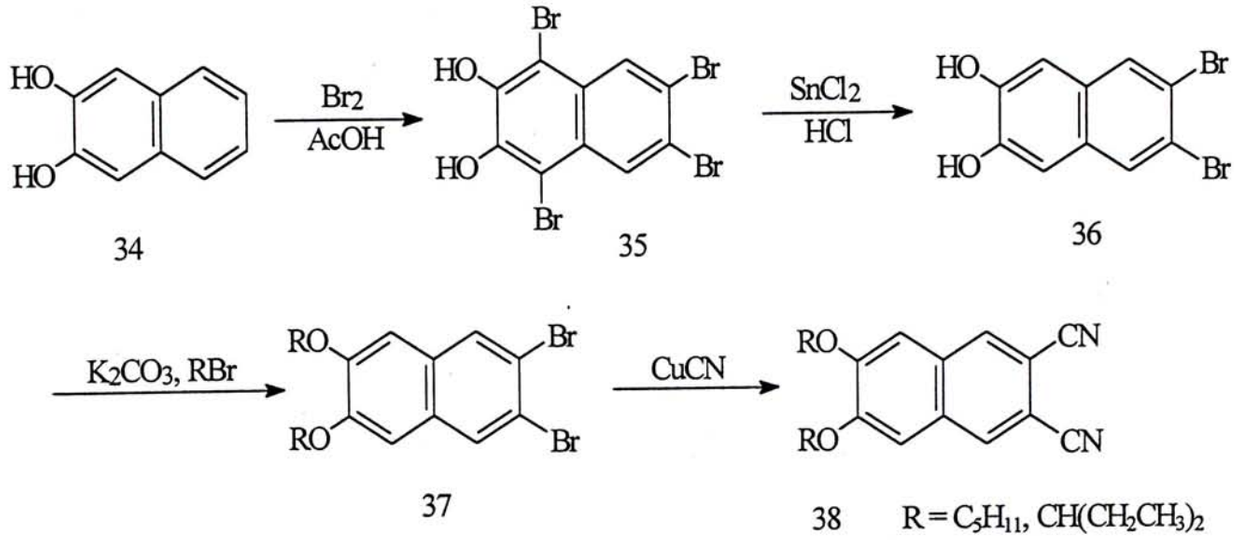
(Scheme 7)

Very recently, Cook *et al.* have reported alternative methods to prepare octaalkyl and octaalkoxy substituted naphthalocyanines.[33] The 1,4-dihexyl-2,3-dicyanonaphthalene (**33**) can be prepared in five steps as shown in Scheme 8. The *o*-dichlorobenzene **28** reacts with the Grignard reagent $C_6H_{13}MgBr$ in the presence of nickel catalyst to give the coupled product **29**. This dihexyl benzene then undergoes benzylic bromination to give compound **30**. Elimination of HBr generates the reactive *o*-quinodimethane derivative **31**, which is trapped with fumaronitrile to give **32.** Treatment of **32** with NBS followed with ^{t}BuOK gives the desired dinitrile **33**.



(Scheme 8)

Compared with the method reported by Hanack *et al.*[24], the synthetic route to 6,7-dialkoxynaphthalonitriles employed by Cook *et al.* is shorter (Scheme 9).[33] Bromination of 2,3-dihydroxynaphthalene (**34**) with bromine in acetic acid yields predominately 1,4,6,7-tetrabromo-2,3-dihydroxynaphthalene (**35**). Selective debromination can be achieved using tin chloride and hydrochloric acid, yielding the dibromo compound **36**. Subsequent *O*-alkylation followed by the Rosenmund-von Braun reaction affords the desired naphthalonitriles **38**.



(Scheme 9)

Compounds **33** and **38** have then been treated with nickel acetate in 1-hexanol with a catalytic amount of DBU to give the corresponding nickel(II) naphthalocyanines.

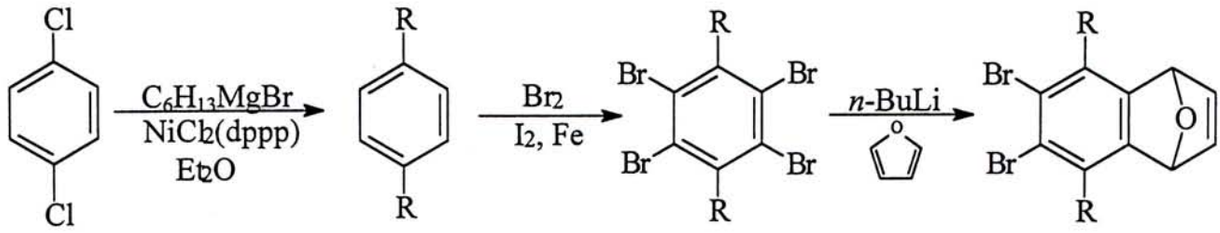
This thesis describes our independent studies on the synthesis and spectroscopic characterizations of differently substituted 2,3-dicyanonaphthalenes and their corresponding zinc 2,3-naphthalocyanines. The aggregation behavior of the zinc Ncs in solution as probed by ^{1}H NMR and UV-Vis spectroscopy will be described. The effects of substituents on the Q band absorption of these marcocycles will also be discussed. Long-chain substituents have been introduced onto the naphthlaocyanine core and the resulting Zn Ncs exhibit liquid crystalline properties as revealed by the DSC measurements and optical microscopic studies. The characteristic fan-shape texture suggests that they are discotic liquid crystals. To our knowledge, these are the first examples of columnar liquid crystals based on 2,3-naphthalocyanine core. The mesogenic properties of these novel marcocycles will also be discussed.

2. Results and Discussion

2.1 Synthesis of Differently Substituted Naphthalocyanines

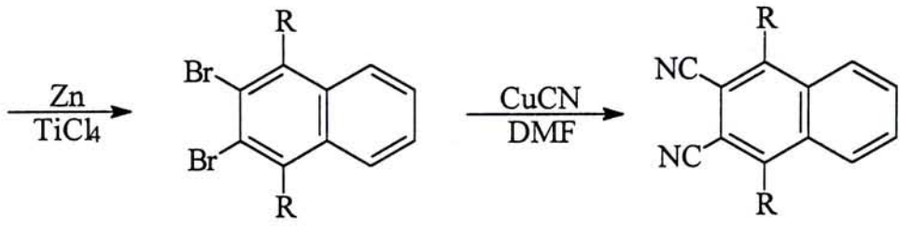
2.1.1 Preparation of substituted dicyanonaphthalenes

The synthetic route to 1,4-dialkyl-2,3-dicyanonaphthalenes is shown in Scheme 10. 1,4-Dihexylbenzene (**40**) was prepared by the nickel-catalyzed coupling reaction of 1,4-dichlorobenzene and *n*-hexylmagnesium bromide. Bromination of **39** and **40** in dichloromethane with a catalytic amount of iron powder and iodine gave the tetrabromobenzenes **41** and **42**, respectively.[34] Treatment of these compounds with *n*-butyllithium generated reactive benzynes which were trapped with furan leading to the formation of epoxides **43** and **44**.[35,36] Upon reductive deoxygenation with zinc and titanium tetrachloride in THF, compounds **43** and **44** were converted to 1,4-dialkyl-2,3-dibromonaphthalenes **45** and **46**, respectively.[35,36] The dinitriles **47** and **33** were obtained by treating **45** and **46** with copper(I) cyanide in DMF under the Rosenmund-von Braun reaction conditions.[35,37]



39 R = CH_3 41 R = CH_3 (75%) 43 R = CH_3 (60%)

40 R = C_6H_{13} (53%) 42 R = C_6H_{13} (83%) 44 R = C_6H_{13} (36%)

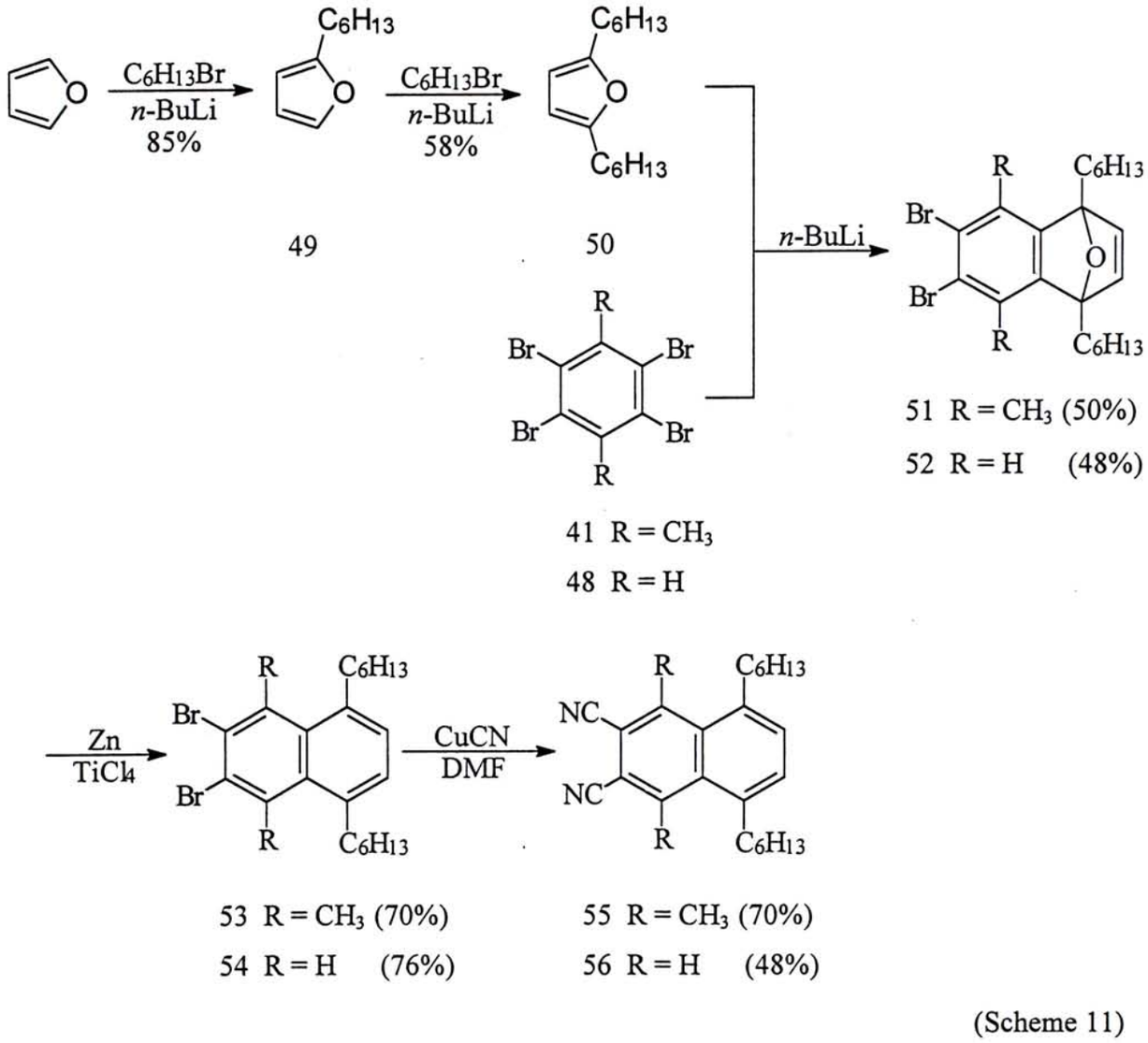


(Scheme 10)

45 R = CH_3 (84%) 47 R = CH_3 (37%)

46 R = C_6H_{13} (84%) 33 R = C_6H_{13} (44%)

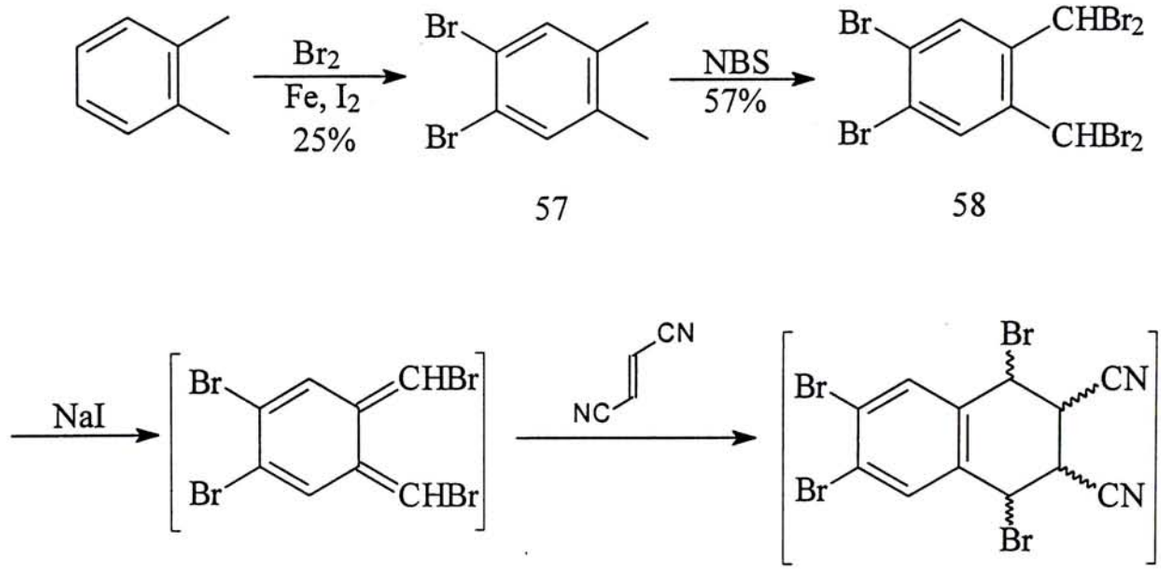
Using a similar strategy, 2,3-dicyano-5,8-dihexyl-1,4-dimethylnaphthalene (**55**) and 2,3-dicyano-5,8-dihexylnaphthalene (**56**) were prepared (Scheme 11). Bromination of 1,4-dibromobenzene in CCl_4 with a catalytic amount of iron and iodine gave 1,2,4,5-tetrabromobenzene (**48**).[36] Treatment of **41** or **48** with *n*-butyllithium and 2,5-dihexylfuran (**50**) led to the formation of the respective Diels-Alder adducts **51** and **52**.[35,36] Reductive deoxygenation of **51** and **52** with zinc and titanium tetrachloride gave the corresponding naphthalenes **53** and **54**,[35,36] which were then converted to the respective dinitriles **55** and **56** by the action of copper(I) cyanide in DMF.[35,37]



(Scheme 11)

Since 3,4-disubstituted furans are not readily available although a substantial progress has been made recently.[38] We employed a different strategy to 6,7-substituted dicyanonaphthalenes which is shown in Scheme 12. The pathway leading to **11** was developed by Luk'yanets *et al.*[28] 1,2-Dibromo-4,5-dimethylbenzene (**57**) was prepared by bromination of *o*-xylene.[39] Benzylic bromination of **57** with *N*-bromosuccinimide in CCl_4 yielded 1,2-bis(dibromomethyl)-4,5-dibromobenzene (**58**),[40] which reacted with fumaronitrile and sodium iodide to give 2,3-dibromo-6,7-dicyanonaphthalene (**11**), through the proposed intermediates **59** and **60**.[28] Compound **11** then underwent aromatic

nucleophilic substitution with thiolate ions RS^- (R = C_3H_7, C_6H_5) to give the corresponding dinitriles **61** and **13**. Compound **13** was described previously,[30] but the use of copper(I) oxide promoted the reactions and greatly improved the reaction yields.



57 58 59 60 11

61 R = C_3H_7 (89%)

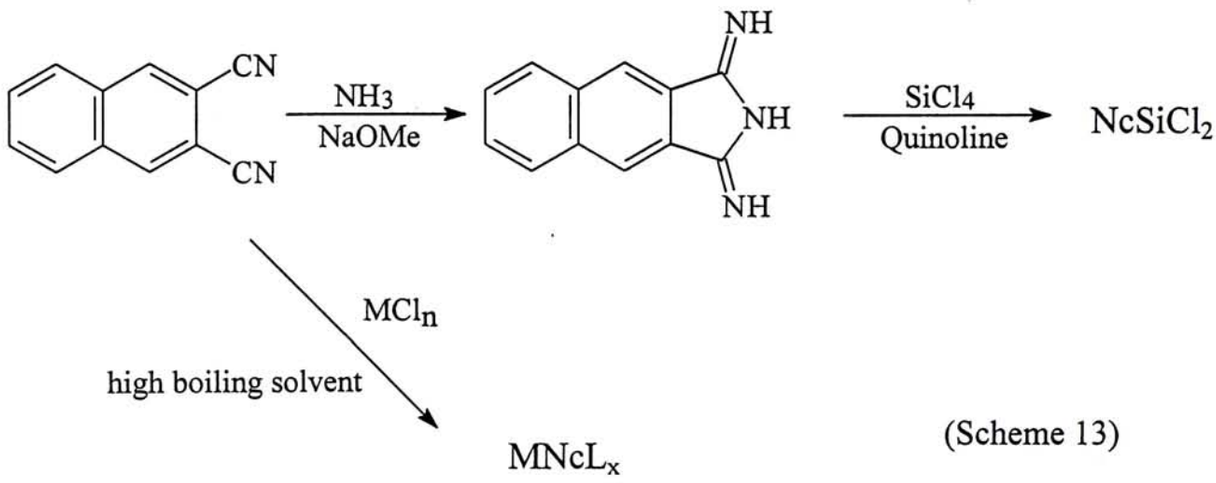
13 R = Ph (84%)

(Scheme 12)

2.1.2 Preparation of octasubstituted naphthalocyaninatozinc(II) complexes

To prepare metal Nc complexes, several methods can be employed. The first one involves the self-condensation of 2,3-dicyanonaphthalene in the presence of a metal halide in high boiling solvent such as quinoline, 1-chloronaphthalene or tetrahydronaphthalene at high temperature (> 200 °C).[18] In some cases, no solvent is

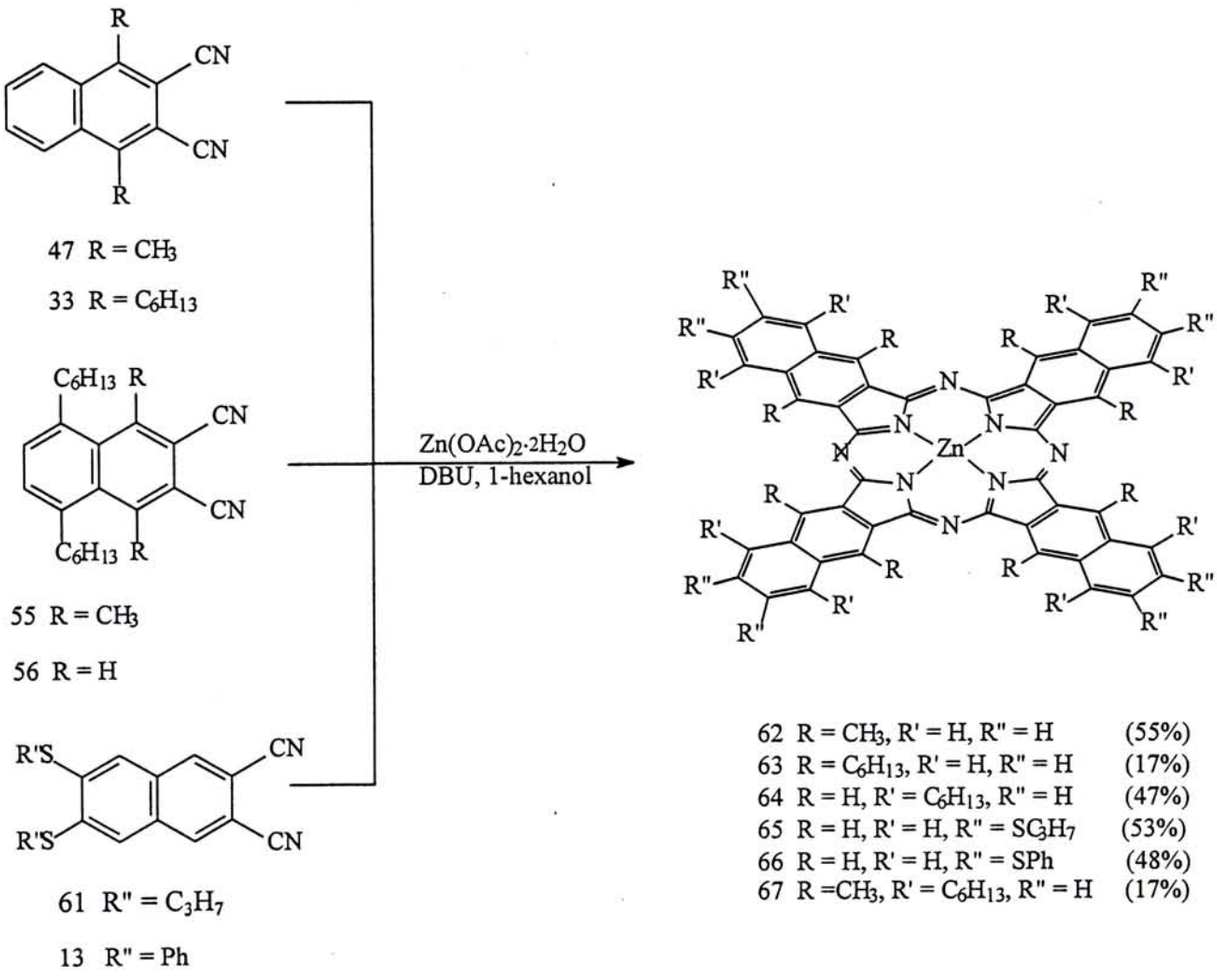
required for the cyclization.[41] Alternatively, 2,3-dicyanonaphthalene can be converted to bisisoindoline prior to cyclization (Scheme 13).[18,42] Although these methods are rather convenient, they have some disadvantages. Firstly, the high boiling solvents are difficult to be removed and at high temperature the 2,3-dicyanonaphthalene may be polymerized. In addition, the bisisoindoline has a poor solubility which hampers the purification procedures, and it has so far been employed to prepare silicon complexes only.[42]



(Scheme 13)

Another commonly used method involves the base-catalyzed cyclization of dinitrile in the presence of a metal salt. We employed this method to prepare the octasubstituted zinc Ncs (Scheme 14). In general, dinitriles and zinc(II) acetate were dissolved in 1-hexanol in a Schlenk tube and the mixture was heated to 90°C. A catalytic amount of DBU was then added and the reaction mixture was heated at 150-160°C for 3-20 h. The cooled mixture was then added dropwise into a mixture of methanol / acetone (1 : 1) to precipitate the zinc Nc complex out. The crude products

could be purified with column chromatography and / or Soxhlet extraction.

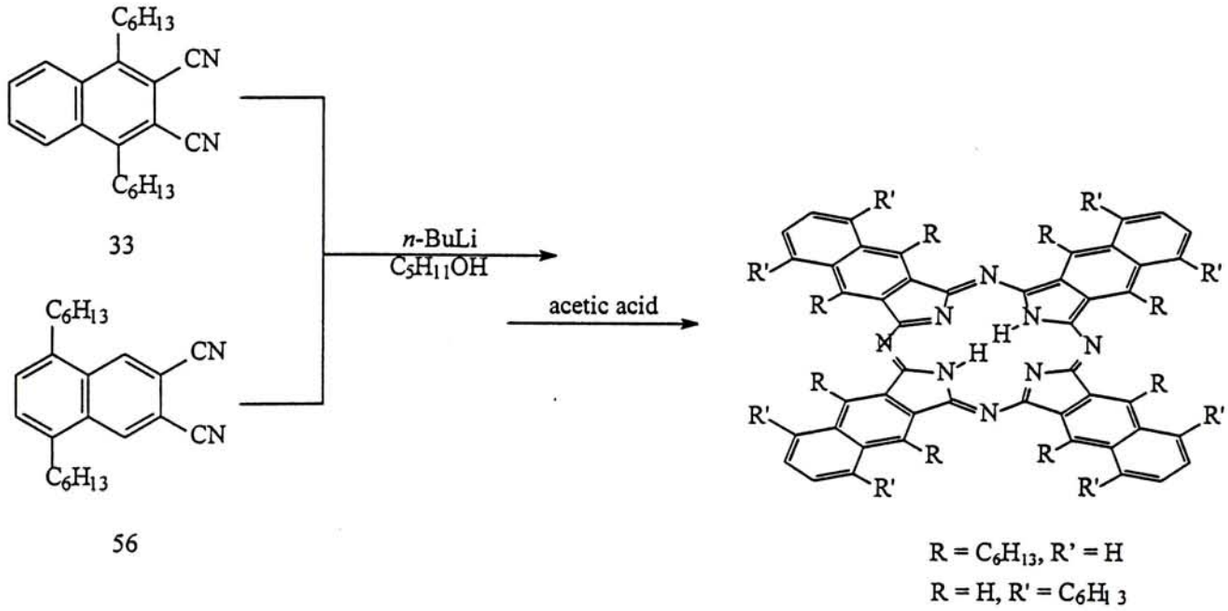


(Scheme 14)

The reaction yields of **62** and **64-66** were moderate (47-55%) while those of **66** and **67** were quite low (17%). For compound **63**, it might be due to the presence of long *n*-hexyl groups at 1,6 positions which hindered the cyclization process. However the reason for low reaction yield of **67** remained unclear since the condensation of **47** to **62** proceeded smoothly.

Apart from the zinc complexes, we also tried to synthesize the metal free Ncs. In general, metal-free naphthalocyanines are prepared by treating dicyanonaphthalenes with either sodium pentoxide in 1-pentanol[43] or lithium metal in a long chain primary alcohol, followed by hydrolysis.[27] Accordingly, dinitriles **33** and **56** were treated with BuLi in

pentanol, then quenched with acetic acid (Scheme 15). The UV-Vis spectra of the crude products showed an intense band at the far red region which could be assigned to the Q band absorption of Ncs. However, these products were not stable in a silica gel column. The color changed from green to red when they were eluted with hexanes / ethyl acetate (5 : 1). As the desired metal-free Ncs could not be purified, this work was not continued.



(Scheme 15)

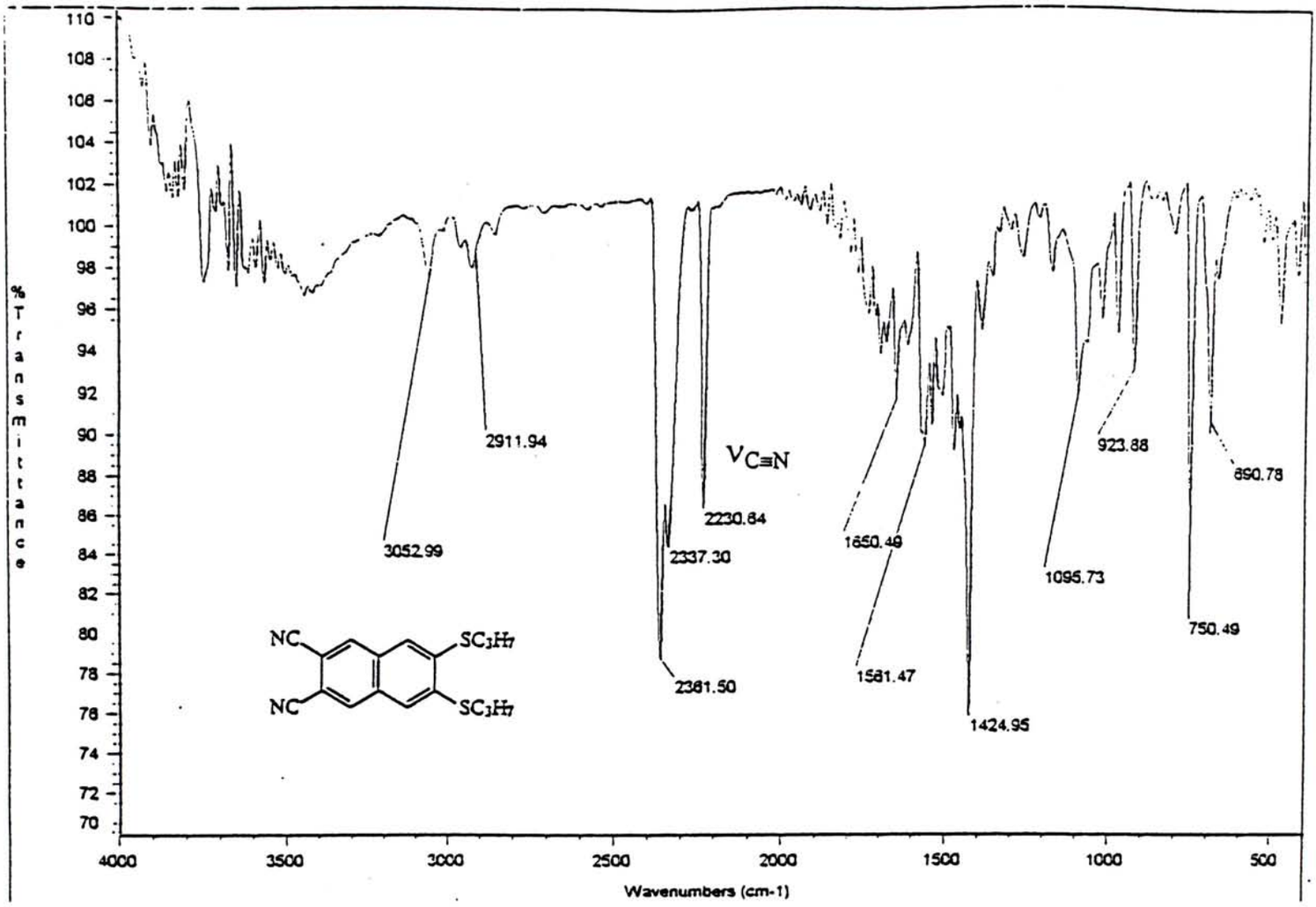
The IR spectra of Ncs **62-67** were recorded and showed that the medium band at *ca.* 2220 cm^{-1} assignable to $\nu_{C\equiv N}$ stretching for the corresponding precursors was absent. This is exemplified in Fig.1, which shows the IR spectra of dinitrile **61** and the corresponding Nc **65**. Due to the high aggregation tendency of these macrocycles, ^1H NMR spectra for all these compounds (except **63** and **64**) in $CDCl_3$ showed only broad signals due to the side chains, while the aromatic core signals were not observed. For compound **62**, it was almost insoluble in common deuterated solvents and therefore no

NMR spectrum could be obtained. For Nc **63**, for which the molecular aggregation appeared to be unimportant, the spectrum recorded in $CDCl_3$ (Fig. 2) exhibited two multiplets at δ 8.70-8.80 and 7.80-7.90 assignable to the AA'BB' system of the aromatic ring. A satisfactory spectrum for **64**, however, could be obtained by changing the solvent to THF-d_8. The spectrum showed, apart from the aliphatic protons' signals, a broad band at δ 9.60 and a relatively sharp band at δ 7.44 which could be attributed to the H_g and H_h aromatic protons, respectively (Fig. 3). Reaction yield and ^1H NMR data for these compounds are tabulated in Table 1.

Table 1 Selected Data for Compounds **62-67**

Compound	Yield (%)	^1H NMR δ (ppm)
62	55	---
63	17	8.70-8.80 (m, 8 H), 7.80-7.89 (m, 8 H), 5.04-5.27 (m, 16 H), 1.94-2.11 (m, 16 H), 1.61-1.77 (m, 16 H), 1.12-1.35 (m, 16 H), 0.85 (quintet, J = 7.0 Hz, 16 H), 0.71 (t, J = 7.0 Hz, 24 H)[a]
64	47	9.60 (br s, 8 H), 7.44 (br s, 8 H), 3.52 (br s, 16 H), 2.10-2.22 (m, 16 H), 1.80-1.92 (m, 16 H), 1.43-1.66 (m, 32 H), 1.05 (t, J = 6.9 Hz, 24 H)[b]
65	53	---
66	48	---
67	17	---

[a] Recorded in $CDCl_3$.
[b] Recorded in THF-d_8 (*ca.* 2.8 x 10^{-3} M)



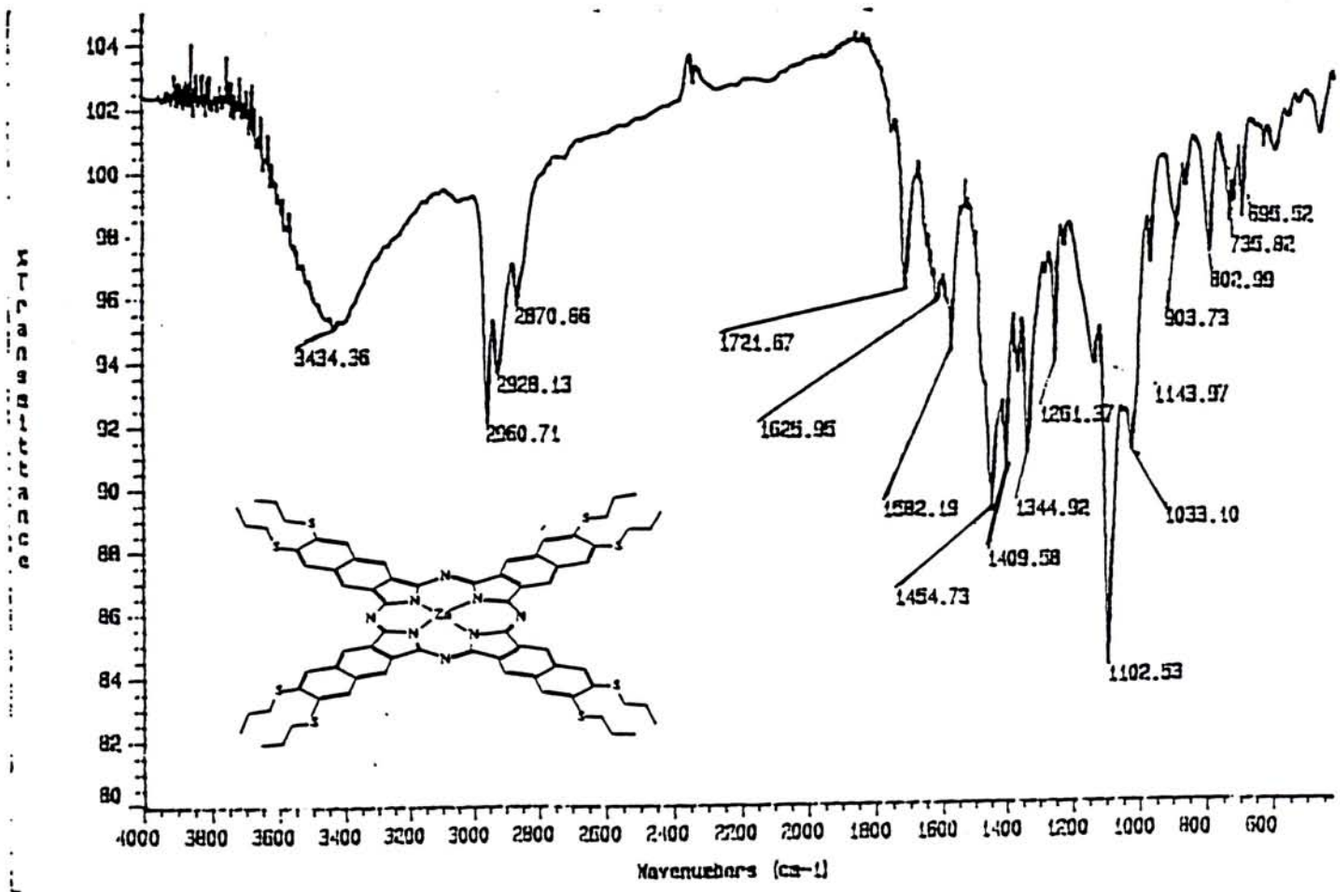


Fig. 1 IR spectra of compounds **61** and **65**.

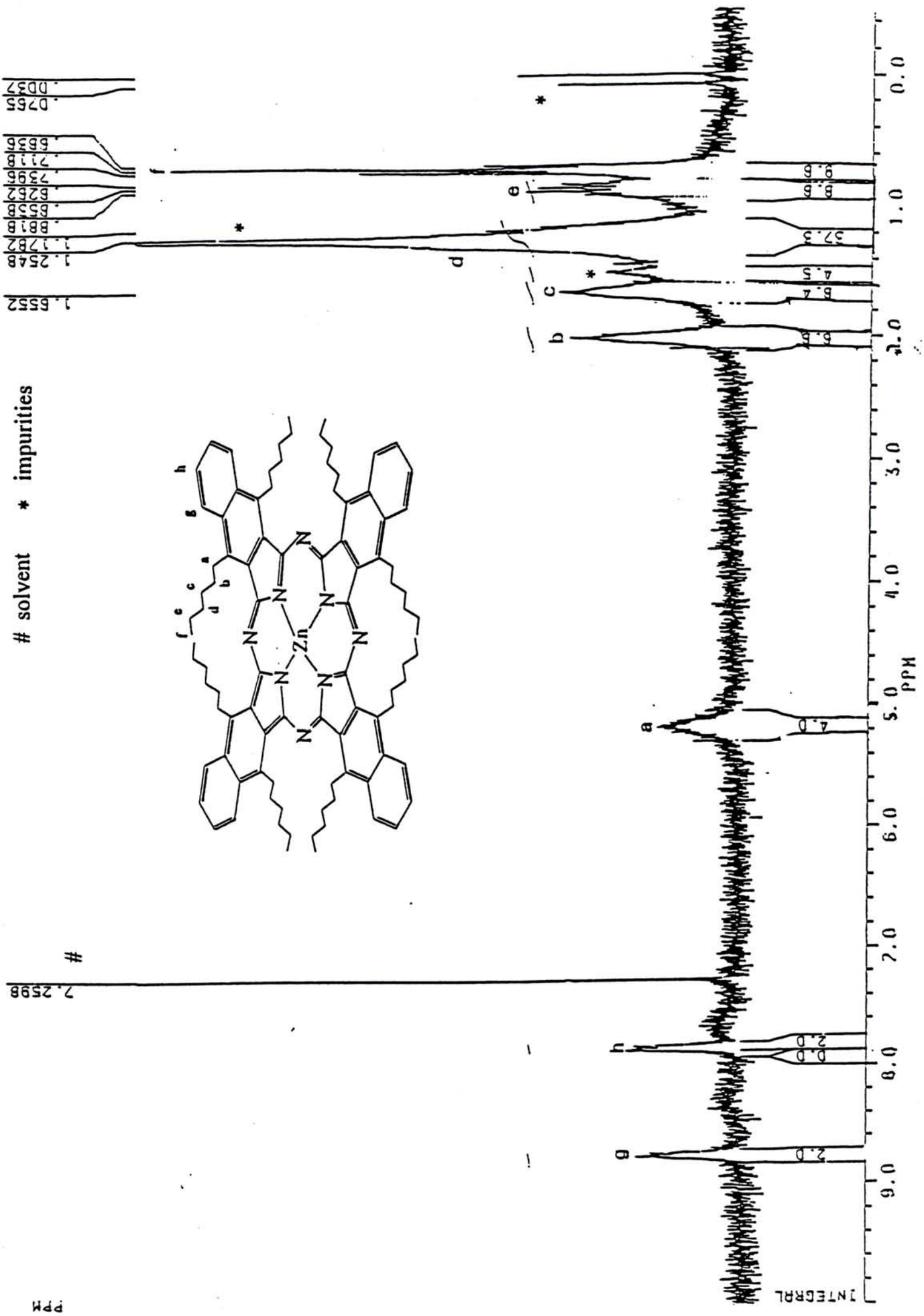


Fig. 2 ^{1}H NMR spectrum of compound **63** in $CDCl_3$.

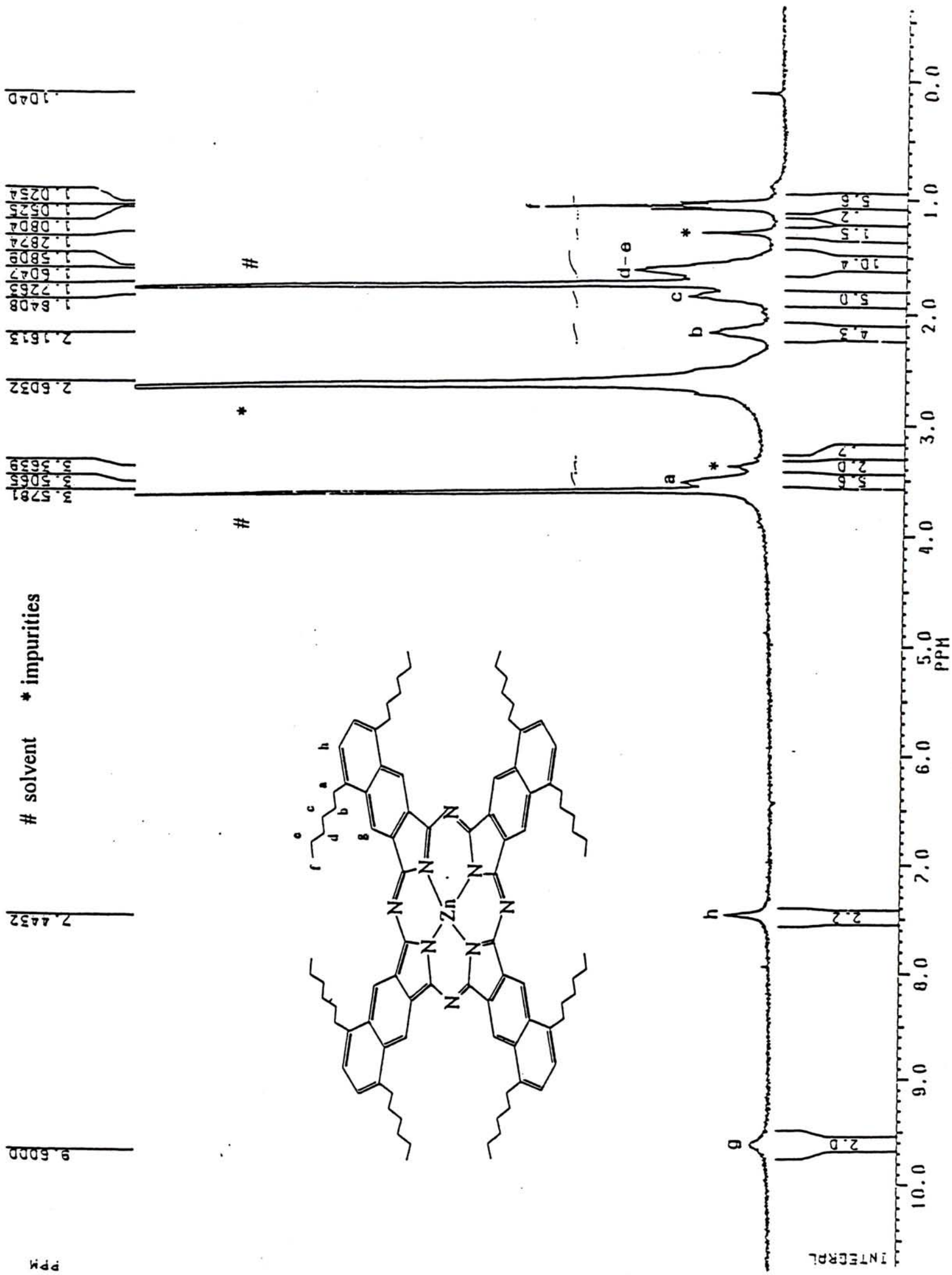


Fig. 3 ^{1}H NMR spectrum of compound **64** in THF-d_8.

The UV-Vis absorption spectra of these complexes displayed a typical Q band and a Soret band, which are attributed to the π-π^* electronic transitions of Nc macrocycles. One to two weaker vibrationally coupled satellite bands were also observed within the Q band region. A representative UV-Vis spectrum of **64** in THF is displayed in Fig. 4. The Q band absorption for all the substituted ZnNc complexes showed a bathochromic shift compared with the unsubstituted analog (ZnNc) (see Section 2.1.4). The data for these ZnNc complexes are summarized in Table 2.

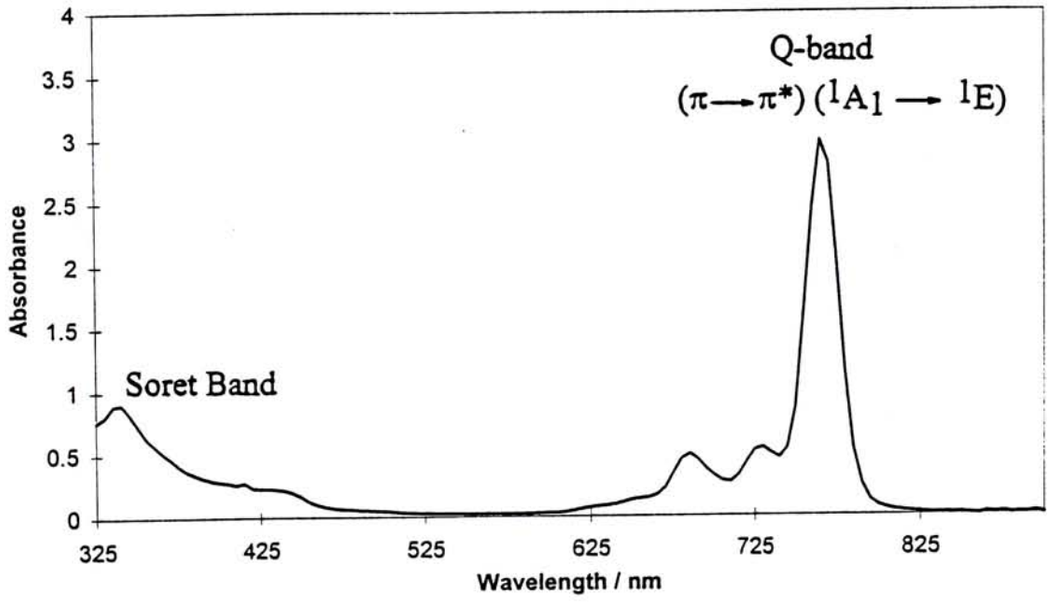


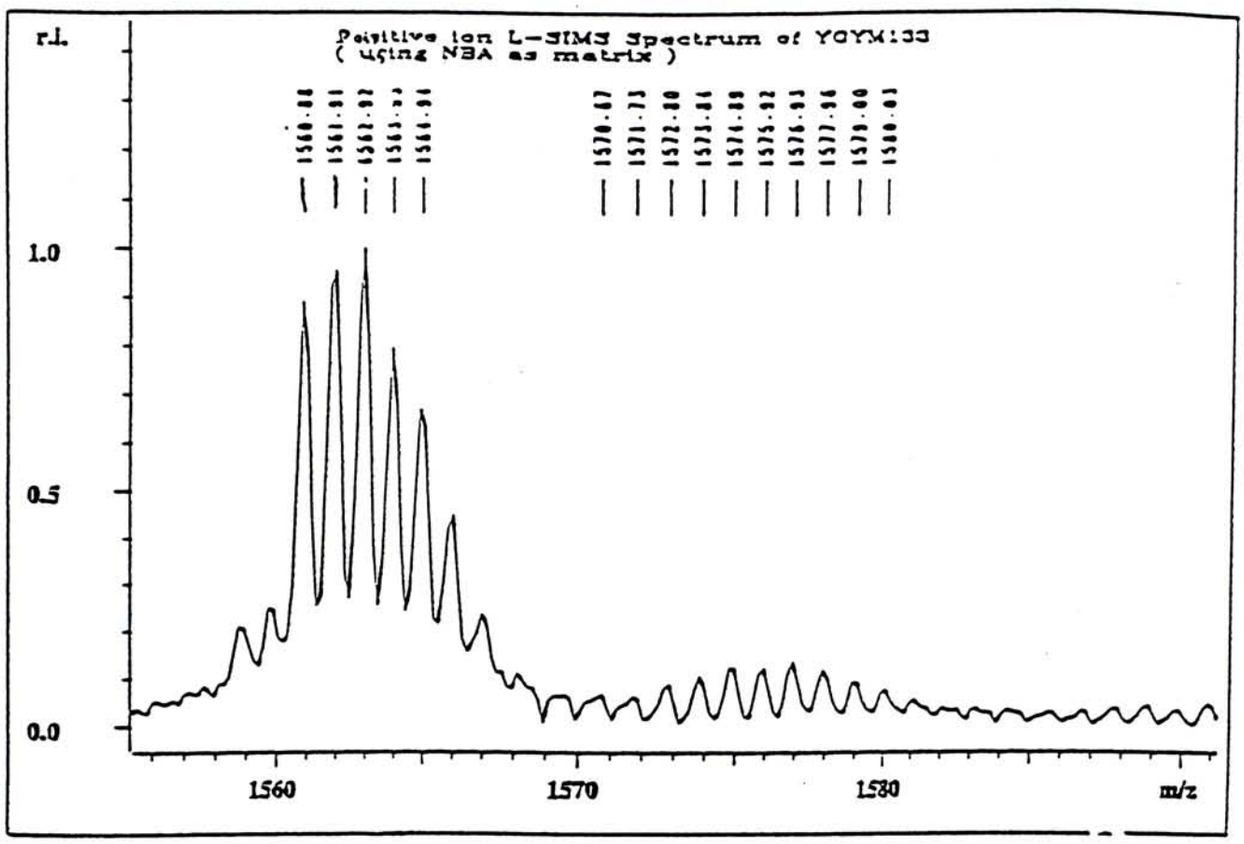
Fig. 4 UV-Vis spectrum of compound **64** in THF.

Table 2 The UV-Vis data for compounds **62-67** in THF

Compound	λ_{max} / nm (log ε)
62	331 (5.29), 709 (4.98), 754 (512), 791 (5.58)
63	722 (4.67), 808 (5.30)
64	338 (4.82), 684 (4.55), 729 (4.60), 776(5.34)
65	355 (4.83), 693 (4.41), 745 (4.59), 778 (5.17)
66	353 (5.16), 694 (4.92), 7.41 (4.90), 779 (5.67)
67	727 (4.75), 812 (5.35)[a]

[a] recorded in hexanes.

The liquid secondary ion mass spectra (LSIMS) of **62-67** were measured with a ultra-high resolution Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. The molecular ion was detected in all cases with the isotopic distribution in good agreement with the corresponding calculated pattern. For example, as shown in Fig. 5, the isotopic pattern of MH^+ species for compound **67** observed (top) well-resemble the simulated spectrum (below). Elemental analyses were also performed for all the new compounds including the Nc complexes. It is commonly observed that the C content is lower than expected for many Pcs and Ncs.[23,44] However, by performing the combustion test at higher temperature (> 1000 °C) and in the presence of excess oxidant, this can sometime be remedied. The mass spectral and analytical results for **62-67** are tabulated in Table 3.



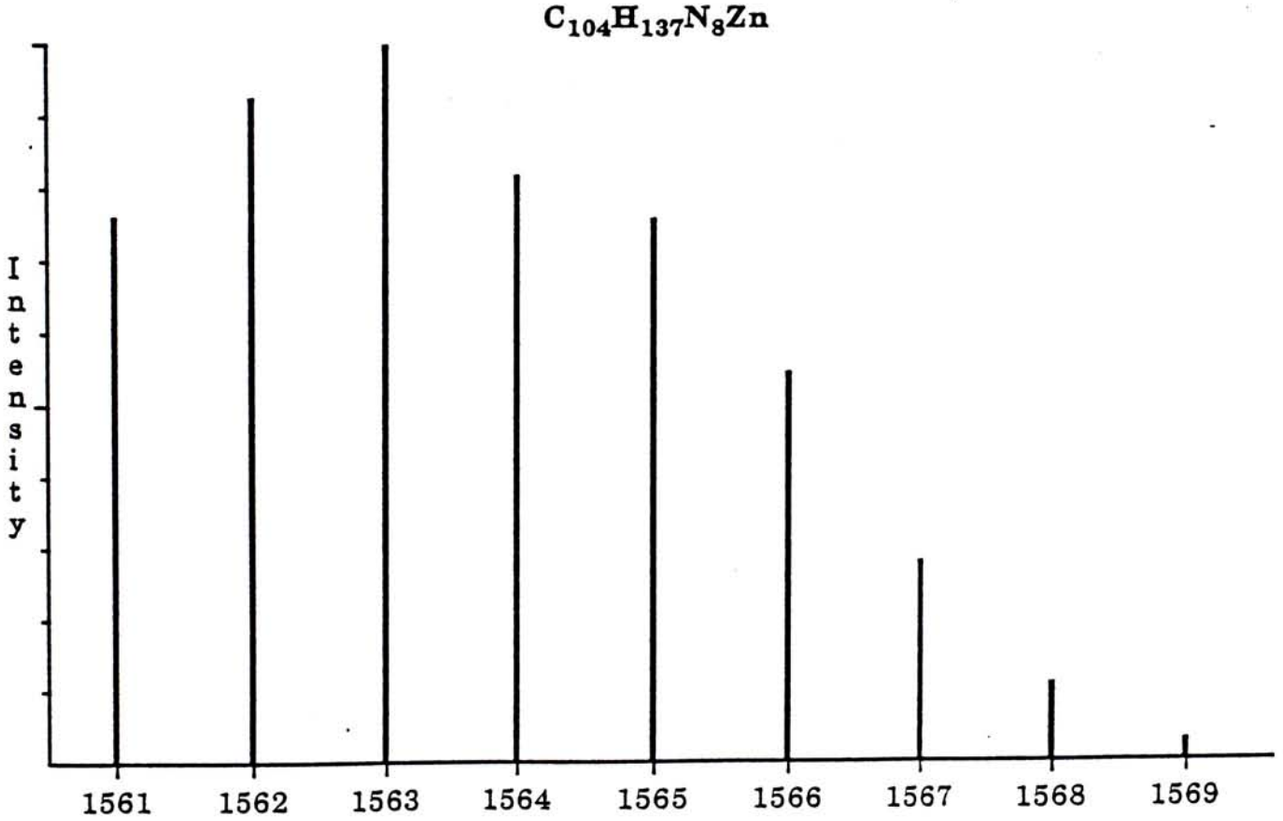


Fig.5 The LSI mass spectrum of **67** showing the isotopic distribution of MH^+ with the corresponding simulated pattern.

Table 3 The mass spectral and analytical data for compounds **62-67**.

Compound	M^+ (m/z)[a]	Analysis[a] (%)		
		C	H	N
62	---	72.25 (72.99)	5.04 (5.07)	11.63 (11.74)[d]
63	1450.90 (1450.89)[b,c]		---	
64	1451.09 (1450.89)[b,c]	78.68 (79.44)	8.38 (8.33)	7.55 (7.72)
65	1370.22 (1370.30)[b,c]	54.91 (55.20)	5.03 (4.63)	6.63 (6.96)[e]
66	1642.09 (1642.17)[b,c]	62.75 (62.54)	3.52 (3.11)	5.67 (5.95)[e]
67	1562.92 (1563.01)[b,c]		---	

[a] Calculated values given in parentheses. [b] By LSI-MS. [c] Mass corresponding to the most abundant isotopic peak of the molecular ion (MH^+). [d] Based on **62**·$2CH_3OH$. [e] Based on compound·$2CHCl_3$.

2.1.3 Aggregation of octasubstituted naphthalocyaninato zinc complexes

It is well-known that phthalocyanines, even in dilute solution, tend to form molecular aggregates such as dimers, trimers, and oligomers.[45-47] Their linear annulated analogs, 2,3-naphthalocyanines, are expected to have higher aggregation tendency because of the more extend π-system. The coupling between the electronic states of two, or more naphthalocyanine units occurs. These aggregated states would have very different characteristics in comparison with the corresponding monomer. The degree of aggregation is largely affected by the nature of the solvent and the concentration of the solution. This aggregation phenomenon imparts difficulties in both the chromatographic purification and characterization processes. The mobility of naphthalocyanines in silica gel columns is greatly reduced, resulting in lost of material and low efficiency in separation. For the spectroscopic characterization, a hysochromic shift of λ_{max} of the Q band with broadening occurs in the UV-Vis spectra of the aggregates. The formation of oligomeric or polymeric aggregates also broadens the ^1H NMR signals for the ring

protons of Ncs. In this section, the aggregation behavior of the substituted 2,3-naphthalocyaninatozinc(II) complexes as studied with UV-Vis sprctroscopy will be discussed.

The UV-Vis spectrum of compound **64** in toluene was found to be concentration dependent (Fig. 6). The Q absorption band at 776 nm was unshifted but the molar absorptivity decreased from 2.48 x 10^5 to 3.94 x 10^4 $M^{-1}cm^{-1}$ as the concentration increased from 2.06 x 10^{-7} to 5.51 x 10^{-5} M. Since further spectral change was not observed at concentrations lower than 2.06 x 10^{-7} M, the spectrum recorded in this concentration could be assigned to the purely monomeric **64**. Assuming that a one step equilibrium between the naphthalocyanine monomer (Nc) and the aggregated species (Nc_n) exists (Eq. 1) and by using the method described by Mataga[48] and Hayashi[45] (see Appendix C) the values of the aggregation number (n) and the aggregation constant (K) for **64** were determined to be 1.57 and 2.48 x 10^3, respectively. The former value suggested that compound **64** tended to form dimer in toluene solution that was analogous to other tetrasubstituted naphthalocyanines.[45] The K value for **64** was however considerably smaller than those for other tetrabutyl counterparts (4 x 10^3-3 x 10^4) under similar conditions. By changing the solvent to THF, the absorption spectrum of **64** was essentially independent of concentration over the range of 5.51 x 10^{-7} to 1.38 x 10^{-5} M. This indicated that aggregation of **64** in THF was not significant in these concentrations.

$$n \cdot Nc \overset{K}{\rightleftharpoons} Nc_n \qquad \text{(Eq. 1)}$$

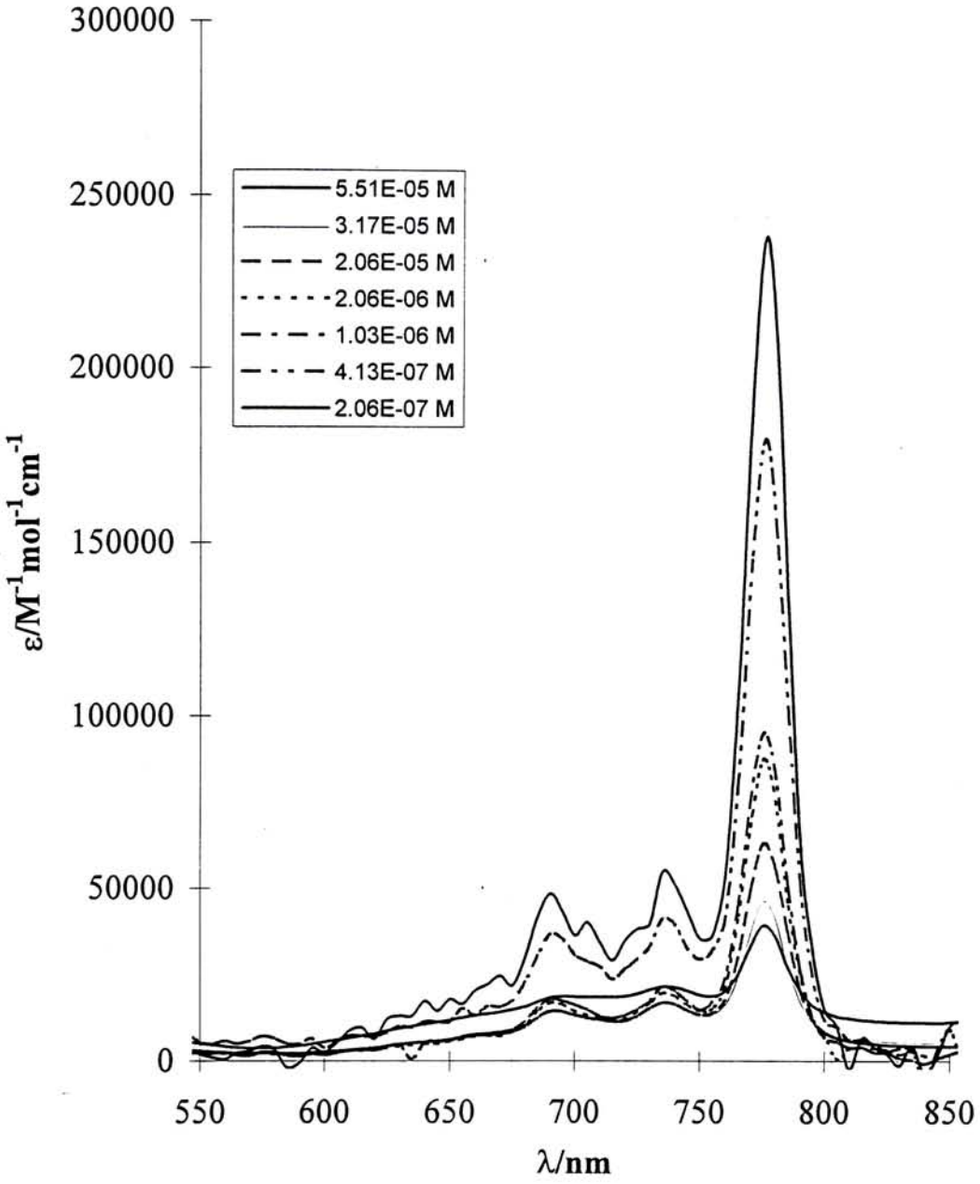


Fig. 6 Concentration dependence of electronic absorption spectra of $ZnNc(C_6H_{13})_8$ (**64**) in toluene

The UV-Vis spectra of compounds **62-67** in hexanes and chloroform were also recorded. The spectrum due to the pure monomeric could only be obtained for compound **63** indicating the lower aggregation tendency of this compound.. The others were found to be concentration dependent and the spectra for the monomeric species could not be obtained even in high dilution. The UV-Vis spectra of compounds **65** and **66** in toluene were also measured in different concentrations. Although the molar absorptivity of the Q band absorption increased on dilution, no absorption spectra assignable to the monomeric species could be observed in both cases. Thus the corresponding n and K values could not be determined under these conditions. However, by using THF as solvent, the values for **66** ($n = 1.97$, $K = 4.40 \times 10^4$) could be calculated from the spectra recorded over the concentration range of 2.14×10^{-7} to 2.14×10^{-5} M. The propylthio analog **65** appeared to have higher aggregation tendency and the spectrum due to the monomer could not be obtained even in high dilution. Thus a relative aggregation tendency could be derived, i.e. **65** > **66** > **64**.

The results obtained from the UV-Vis spectroscopic studies was in accord with the results based on the ^{1}H NMR data. The ^{1}H NMR spectra of **64-66** in $CDCl_3$ showed only broad signals due to the side chains, while the aromatic core signals were not observed. By changing the solvent to THF-d_8, only compound **64** could give a satisfactory spectrum. These observations also suggested that the aggregation tendency of these compounds followed the order **65**, **66** > **64**.

2.1.4 Effects of substituents on the electronic spectra of 2,3-naphthalocyaninatozinc(II) complexes

Very recently, Cook *et al.* have synthesized a series of octasubstituted 2,3-naphthalocyaninatonickel(II) complexes.[33] In their studies, they have found that the nature and position of substituents at the peripheral sites could have substantial influences on the Q band absorptions. The results are very similar to what we found and can support our discovery.

The UV-Vis spectra of compounds **62-66** in DMSO and THF were obtained and a comparison of the Q band absorptions is given in Table 4. Since compound **67** is a hexadecasubstituted naphthalocyanine and is virtually insoluble in DMSO, its data is not included.

Table 4 λ_{max} of the Q band of 2,3-naphthalocyaninatozinc(II) complexes

Compound	λ_{max} of Q band in DMSO (nm)	$\Delta\lambda_{max}$ (nm)[a]	λ_{max} of Q band in THF (nm)	$\Delta\lambda_{max}$ (nm)[b]
ZnNc	770	0	756	0
62	800	30	790	34
63	816	46	808	52
64	811	41	776	20
65	791	21	778	22
65	785	15	779	23

[a] Bathochromic shift with respect to the λ_{max} of unsubstituted (2,3-naphthalocyaninato)zinc(II) (ZnNc) taken from ref. 43.

[b] Bathochromic shift with respect to the λ_{max} of unsubstituted (2,3-naphthalocyaninato)zinc(II) (ZnNc) taken from ref. 49.

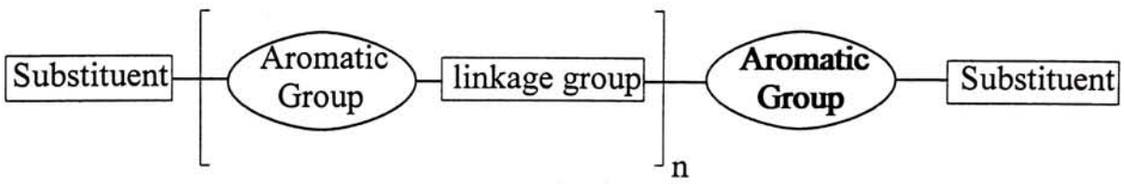
In the case of using DMSO as solvent, we found that substituents located at the 1,6 positions (e.g. **62** and **63**) cause the largest bathochromic shifts ($\Delta\lambda_{max}$ equal to 30 nm and 46 nm, respectively). Substitution at the 3,4-positions (e.g. **65** and **66**) induces only minor perturbations of the Q band energy ($\Delta\lambda_{max}$ equal to 21 nm and 15 nm, respectively). Substituents at the 2,5-positions (e.g. **64**) cause a red shift of 41 nm which lies between the previous two cases. By comparing the $\Delta\lambda_{max}$ between compounds **63** and **64**, in which both of them are substituted with the same side chain (*n*-hexyl) but at different positions, it is clear that substituents nearer to the porphyrazine ring cause larger bathochromic shifts. Besides the location of the substituents, the size of the substituents will also affect the extent of bathochromic shift. Taking compounds **62** and **63** as example, they have the same substitution pattern, but one with methyl groups and the other with *n*-hexyl groups. As the size of the substituents in **63** is larger, we found that it induces a larger bathochromic shift of the Q band absorption. Similar results can be obtained by comparing the Q band λ_{max} of unsubstituted ZnNc and compound **62**. Substitution of H with larger methyl groups also shifts the λ_{max} by 30 nm.

When THF was used as solvent, the Q band of all of these compounds was blue-shifted as compared with those recorded in DMSO. But similar effects induced by substitution was still observed.

2.2 Synthetic Study of Liquid Crystals Based on a 2,3-Naphthalocyanine Core

Liquid crystals constitute a fascinating state of condensed matter between crystalline solids and isotropic liquids. They exhibit rheological behavior similar to that of liquids and anisotropic physical properties similar to those of crystalline solids. Their dual nature and fast response to electric, magnetic, and surface forces have rendered this materials useful in various disciplines. Besides being used in the familiar numeric displays and temperature sensors, liquid crystals also play an important role in the development of high resolution TV displays, projection systems, optical computing, and high strength fibers.[50]

At present there is no way of predicting with certainty whether or not a given molecule will exhibit liquid crystal mesophases. However, the presence of common structural features in the majority of thermotropic liquid crystal mesogens makes possible certain generalizations regarding the types of molecules most likely to show liquid-crystalline behavior. The two structural features that appear essential are (1) the constituent molecules must be elongated and (2) they must be rigid. This can be represented schematically as



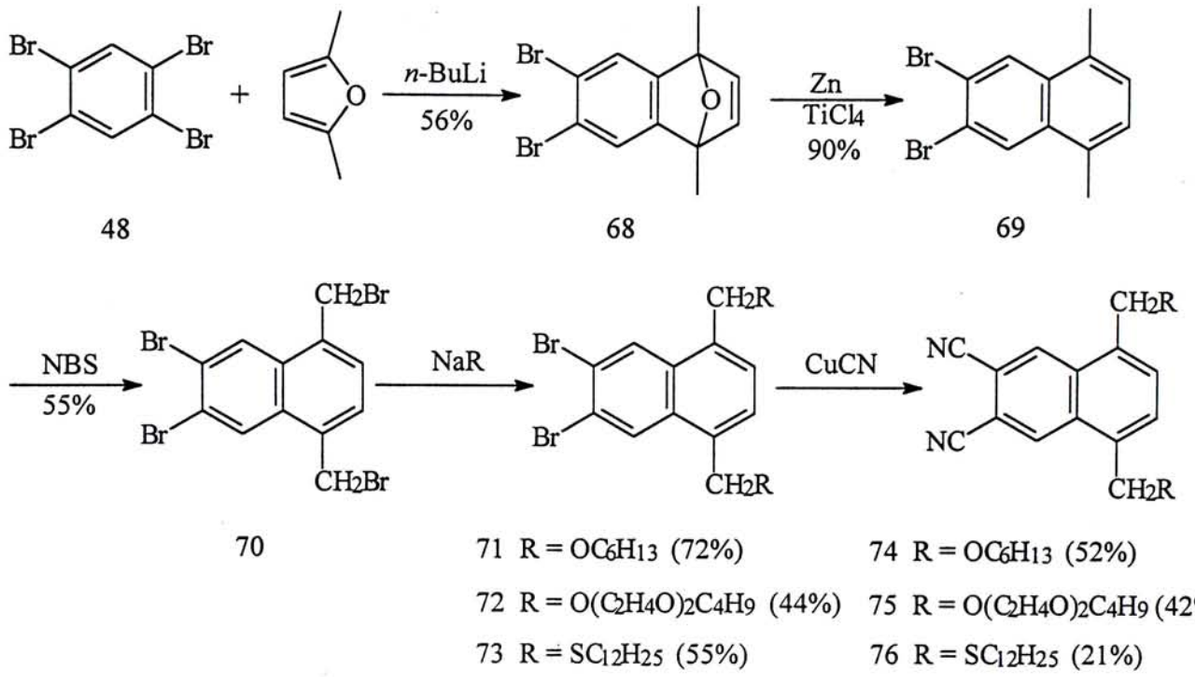
with n = 0, 1, or 2. Many of these molecules exhibit nematic and smectic mesophases.[51] When n = 0 and the aromatic group is changed to a large conjugated macrocycle (such as phthalocyanine), this molecule may behave as a liquid. From the previous reports on liquid crystalline phthalocyanines,[52] it was shown that phthalocyanines substituted with long flexible hydrocarbon side chains can form the so-called discotic mesophases at elevated temperatures. These mesophases are mainly hexagonally ordered.

Owing to the success of the synthesis of octasubstituted naphthalocyaninatozinc(II) complexes, we then extended these synthetic routes to Zn Ncs with long-chain substituents. With extra fused benzene rings, 2,3-naphthalocyanines with appropriate substitution may also exhibit hexagonal discotic mesophases. In this section, the synthesis, spectroscopic characterization, and mesomorphic properties of some liquid crystalline naphthalocyanines are described. It is worth noting that columnar liquid crystallines based on a 2,3-Nc core have not been reported previously.

2.2.1 Preparation of dicyanonaphthalenes substituted with long side chains

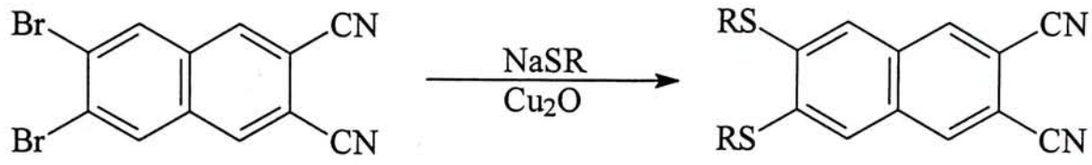
The 5,8-disubstituted dicyanonaphthalenes **74**, **75**, and **76** were synthesized from the key compound **70**. The synthetic route is shown in Scheme 16. Treatment of compound **49** with n-butyllithium and 2,5-dimethylfuran gave the epoxide **68**,[35,36] which underwent deoxygenation yielding the dibromonaphthalene **69**.[35,36] Benzylic bromination of **69** afforded the 5,8-bis(bromomethyl)-2,3-dibromonaphthalene (**70**). Alkoxylation of **70** introduced two long-chain substituents to give compounds **71** and **72**.[53] Compound **70** was also coupled with dodecylthio ion yielding compound **73**. The

dinitriles **71**, **72**, and **73** were then converted to the corresponding dicyanonaphthalenes **74**, **75**, and **76**, respectively by the Rosenmund-von Braun reaction. The reaction yield of **76** was relatively low compared with those of **74** and **75**. The conversion rate was also slow as monitored by TLC.



(Scheme 16)

The 6,7-disubstituted 2,3-dicyanonaphthalenes **77** and **78** were prepared by the aromatic nucleophilic substitution of **11** with thiolates $NaSC_8H_{17}$ and $NaSC_{12}H_{25}$, respectively (Scheme 17). By comparing with the reaction yield for the propylthio analog **61** (89%), it can be seen that as the size of the thiolate ion increases, the reaction yield is lower.



11

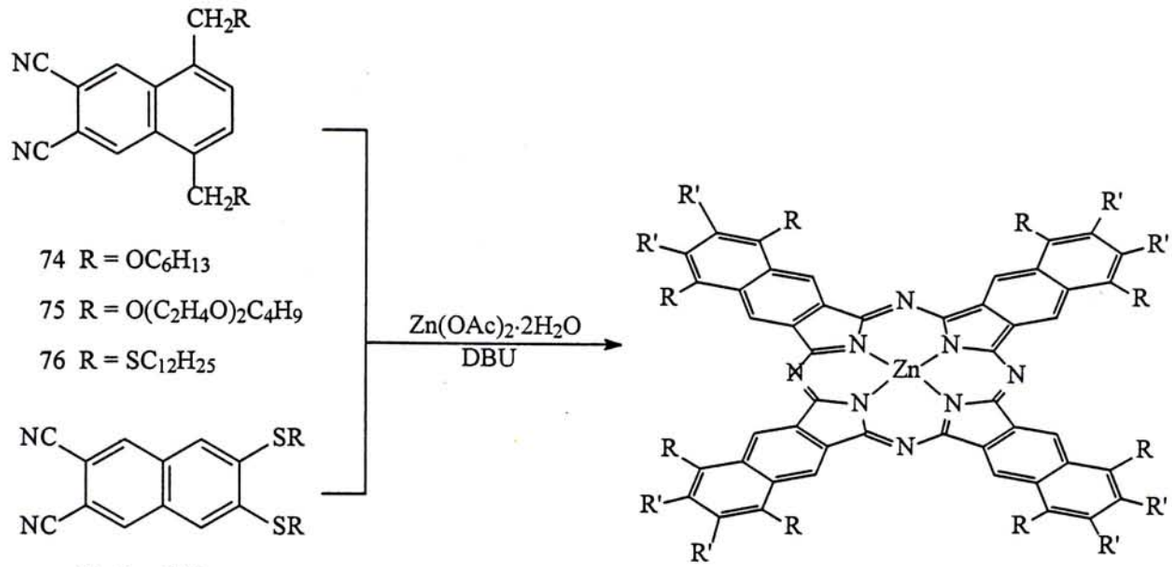
77 R = C_8H_{17} (49%)

78 R = $C_{12}H_{25}$ (30%)

(Scheme 17)

2.2.2 Preparation of liquid crystallines 2,3-naphthalocyaninatozinc(II) complexes

By using the same procedure described in Section 2.1.2 for the preparation of naphthalocyaninatozinc(II) complexes, the substituted dicyanonaphthalenes **74-78** were treated with zinc(II) acetate and a catalytic amount of DBU in 1-hexanol giving the corresponding octasubstituted naphthalocyaninatozinc(II) complexes **79-83** (Scheme 18). The reaction yields are satisfactory (36-60%) and all of these compounds are highly soluble in common organic solvents and therefore can be purified by column chromatography. They are deep green solids and decompose readily at high temperature (>300°C).



79 R = $CH_2OC_6H_{13}$, R' = H (60%)
80 R = $CH_2O(C_2H_4O)_2C_4H_9$, R' = H (36%)
81 R = $CH_2SC_{12}H_{25}$, R' = H (45%)
82 R = H, R' = SC_8H_{17} (49%)
83 R = H, R' = $SC_{12}H_{25}$ (42%)

Scheme 18

The ^1H and ^{13}C NMR spectra of compounds **79-83** in benzene-d_6 showed only broad signals due to the aliphatic side chains, while the aromatic signals were not observed. This is due to the strong aggregation tendency of these compounds. However, the addition of pyridine could solve this problem and satisfactory spectra were obtained showing that pyridine is able, if not completely, to disrupt the molecular interactions. The ^1H NMR spectra of compounds **79** and **82** in benzene-d_6 / pyridine-d_5 (3 : 1) are displayed in Figs. 7 and 8, respectively. In both spectra, two very downfield broad signals were observed which can be ascribed to H_1 and H_3 (or H_2 for **82**). Comparing with the spectra of the corresponding dicyanonaphthalenes, H_1 protons' signal experiences the most downfield shift (*ca.* 1.4-1.5 ppm). The H_2 protons' signal shifts only by *ca.* 0.6 ppm while the signal due to H_3 protons is only marginally shifted (*ca.* 0.2

ppm). The benzylic protons' resonance is also shifted downfield by 0.3-0.4 ppm and the signals for the aliphatic side chains remain almost unchanged. These chemical shift changes arise from the large ring current of Nc macrocycle, and the aromatic protons at the 1,6-positions lie closest to the central core and therefore are most susceptible by the ring current. The reaction yields, ^{1}H and ^{13}C NMR data for compounds **79-83** are summarized in Table 5.

Table 5 Selected data for compounds **79-83**.

Compound	Yield (%)[a]	^{1}H NMR δ (ppm)[a]	^{13}C NMR δ (ppm)[a]
79	60	10.00 (br s, 8 H), 7.92 (br s, 8 H), 5.39 (br s, 16 H), 3.84 (br s, 16 H), 1.87-1.97 (m, 16 H), 1.57-1.70 (m, 16 H), 1.15-1.45 (m, 32 H), 0.83 (t, *J* = 6.8 Hz, 24 H).	---
80	36	10.08 (br s, 8 H), 7.85 (br s, 8 H), 5.42 (br s, 16 H), 4.03 (br s, 16 H), 3.93 (br s, 16 H), 3.79-3.83 (m, 16 H), 3.56-3.60 (m, 16 H), 3.29 (t, *J* = 6.4 Hz, 16 H), 1.38-1.48 (m, 16 H),1.24-1.34 (m, 16 H), 0.78 (t, *J* = 7.3 Hz, 24 H).	153.3, 136.2, 135.2, 131.8, 125.6, 118.7, 72.1, 71.3, 71.2, 70.8, 70.7, 70.3, 32.2, 19.6, 14.1
81	45	10.07 (br s, 8 H), 7.55 (br s, 8 H), 4.53 (br s, 16 H), 2.72 (br s, 16 H), 1.89 (br s, 16 H), 1.45 (br s, 16 H), 1.20 (br s, 128 H), 0.78-0.81 (m, 24 H)	---
82	49	9.47 (br s, 8 H), 8.20 (br s, 8 H), 3.22 (br s, 16 H), 1.97 (br s, 16 H), 1.61 (br s, 16 H), 1.35 (m, 64 H), 0.93 (t, *J* = 6.3 Hz, 24 H)	153.2, 137.5, 135.8, 132.3, 127.7, 120.8, 33.9, 32.3, 29.9 (two signals), 29.8, 29.2, 23.2, 14.4
83	42	9.53 (br s, 8 H), 8.27 (br s, 8 H), 3.29 (br s, 16 H), 2.05 (br s, 16 H), 1.70 (br s, 16 H), 1.20-1.60 (m, 128 H), 0.90 (t, *J* = 6.7 Hz, 24 H)	153.3, 137.6, 135.8, 132.4, 127.3, 120.9, 34.0, 32.4, 30.3, 30.3, 30.0, 29.3, 23.2, 14.4

[a] The ^{1}H and ^{13}C NMR spectra were recorded in C_6D_6 / C_5D_5N (3 : 1).

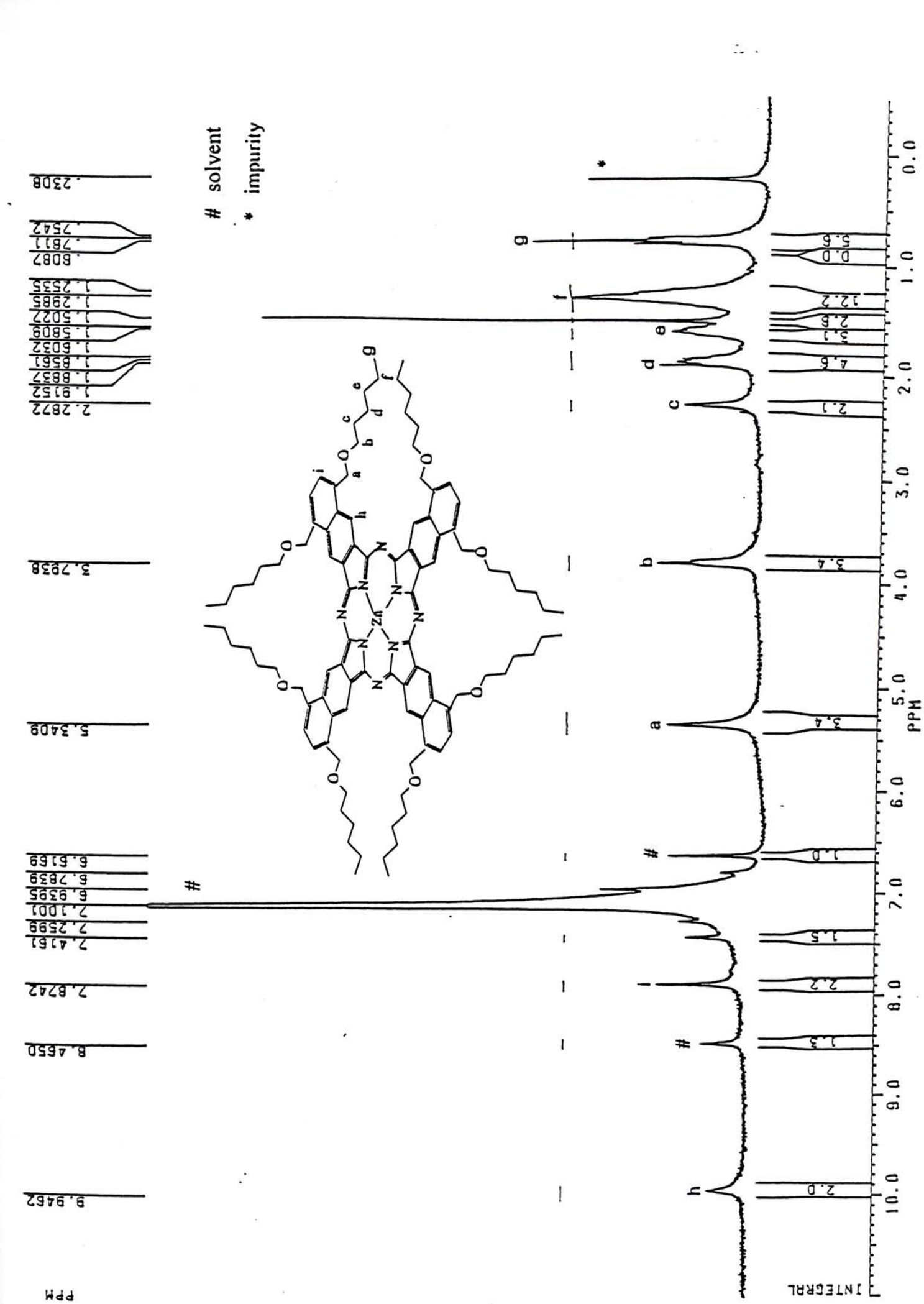


Fig .7 ^{1}H NMR spectrum of compound **79** in C_6D_6 / C_5D_5N (3 :1).

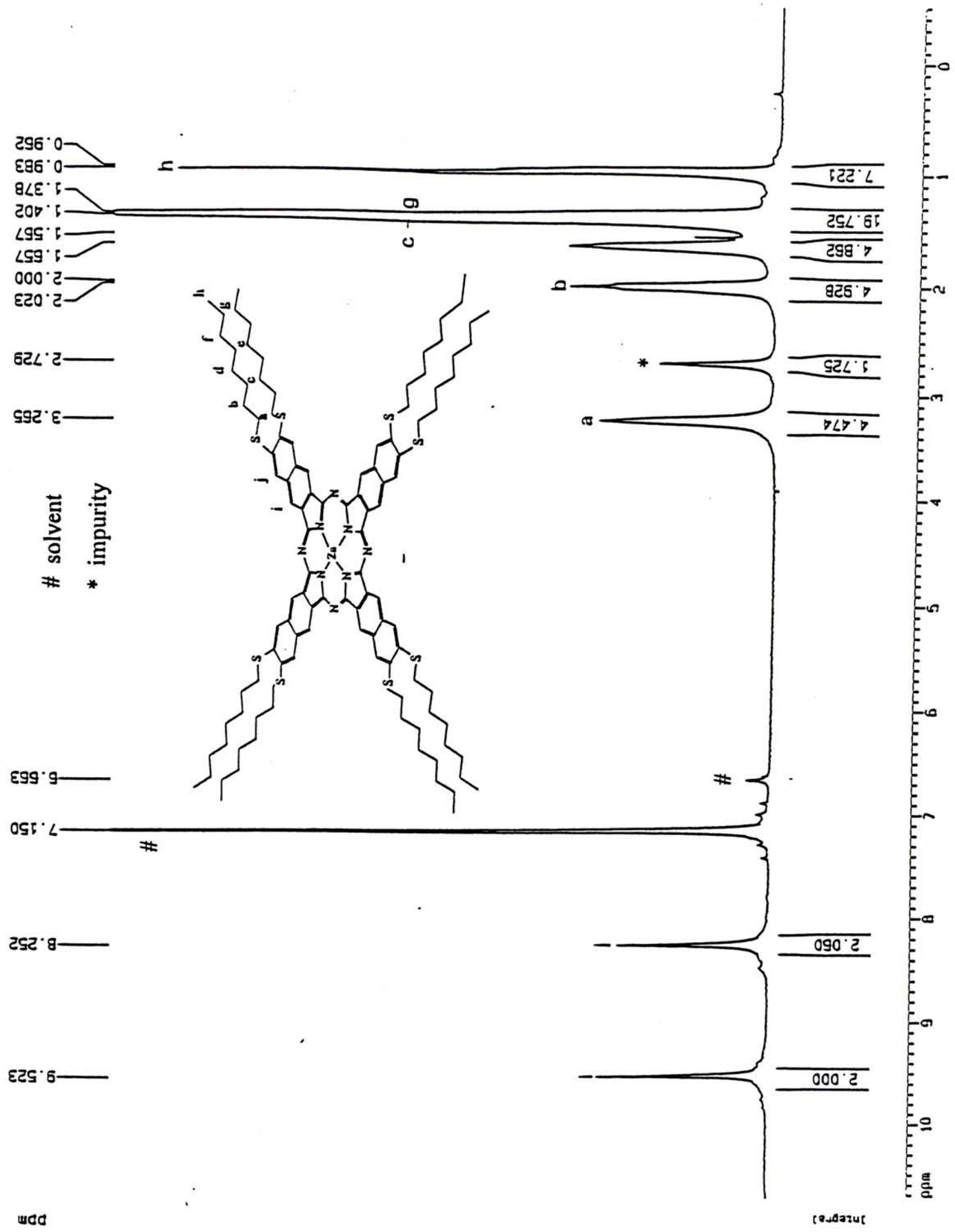


Fig. 8 ^{1}H NMR spectrum of compound **82** in C_6D_6 / C_5D_5N (3 : 1).

The UV-Vis absorption spectra of these complexes also displayed a typical Q band and a Soret band. The former is red-shifted for all complexes when compared with that of unsubstituted ZnNc. It is noteworthy that the extinction coefficients of both Q and B bands for all these compounds (except **81**) are higher than those of the compounds mentioned in Section 2.1, which may indicate that the degree of aggregation is smaller for these long-chain substituted Ncs. Table 6 listed the UV-Vis data for compounds **79-83**.

Table 6 The UV-Vis data for compounds **79-83** in THF

Compound	λmax / nm (log ε)
79	336 (5.50), 676 (5.30), 721 (5.27), 756 (6.13)
80	336 (5.32), 677 (5.10), 722 (5.09), 757 (5.93)
81	340 (4.32), 683 (4.11), 728 (4.12), 765 (4.87)
82	350 (5.62), 696 (5.31), 737 (5.36), 779 (6.03)
83	347 (5.49), 697 (5.13), 743 (5.16), 780 (5.92)

By introducing longer side chains onto the peripheral sites of the naphthalocyanine core, we found that it could prevent the Nc molecules to form aggregates and so purifications of these compounds by column chromatography could be performed readily.

2.2.3 Characterization of the liquid crystals

The mesophase behavior of **79**, **80**, **82** and **83** was studied by differential scanning calorimetry (DSC) and polarized optical microscopy. The results are listed in Table 7 and the DSC thermograms of **79**, **80**, and **83** are shown in Figs. 9, 10, and 11, respectively. The DSC thermograms of **79** and **83** showed only a single endothermic peak within the range of 25-300°C, corresponding to the crystalline to mesophase transition. No transition peak was observed for **82** but an inclined straight line was obtained. No well-defined transition peak was found for **80**, which is soft and rubbery at room temperature. Upon heating above the transition temperature or *ca.* 150°C in the case of **80**, the melt of these compounds was very viscous and the birefringence formed slowly as viewed through a polarized microscope. The optical texture of the mesophase was fan-shape, which is characteristic of the hexagonal discotic columnar mesophase and is commonly observed for substituted phthalocyanines.[54] Two photographs of **80** obtained from the polarized microscope are displayed in Fig. 12. As the isotropic phase could not be reached up to 300°C at which decomposition of the compounds began, the mesophase was observed on heating from their crystalline phase rather than cooling from the isotropic phase. The samples were thus annealed at elevated temperature for 2-4 days prior to microscopic investigation. It is worth noting that the analogous phthalocyanines usually have clearing temperature lower than 250°C.[54] The extraordinary high isotropization temperature of naphthalocyanines **79**, **80**, **82**, and **83** may associate with the stronger π-π stacking interactions among the molecules.

Table 7 Thermal behavior of 82 and 86

Compound	Transition	T / °C	ΔH / KJ mol^{-1}
79	K-D_h	133	16.7
83	K-D_h	100	52.1

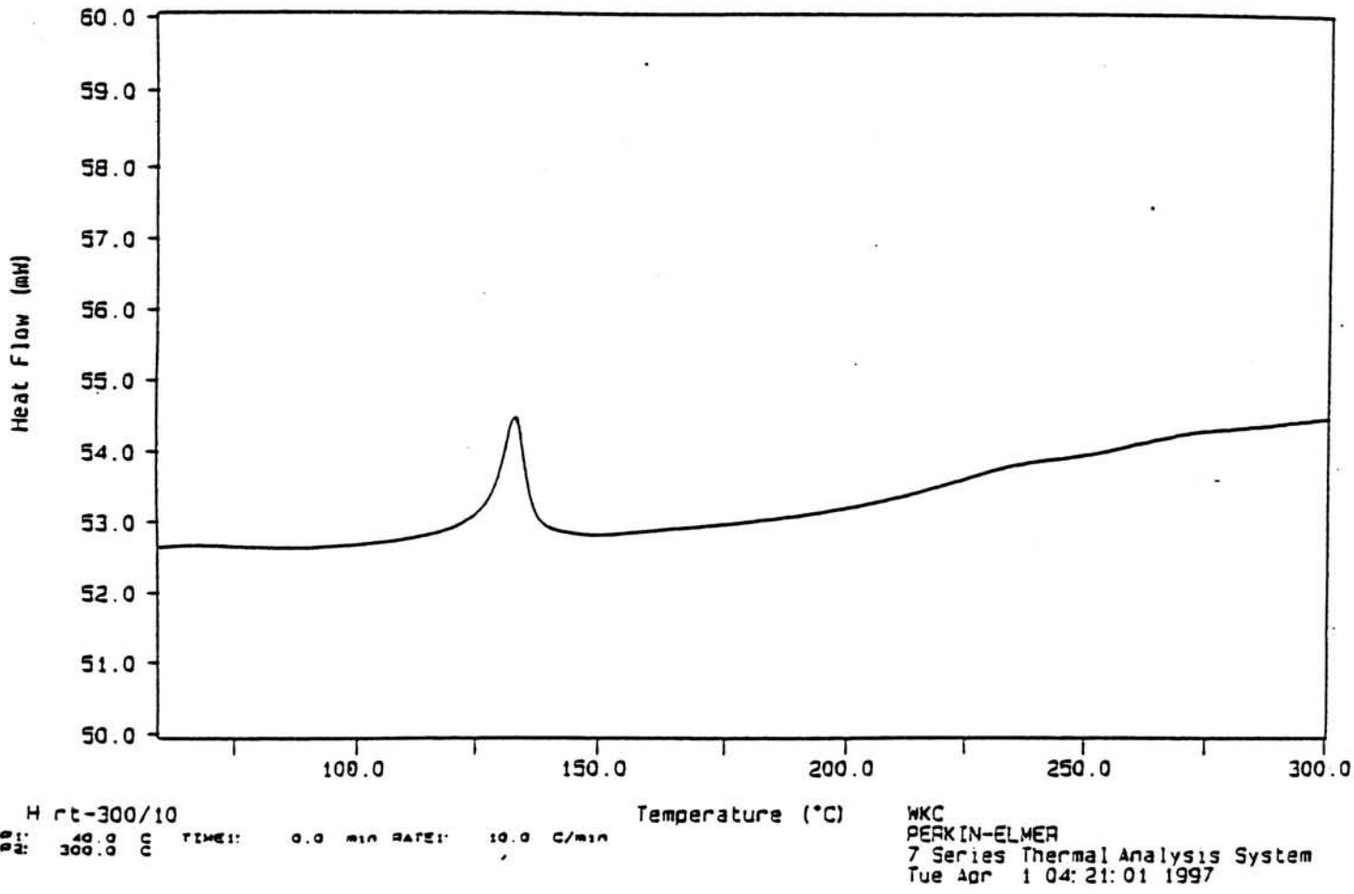


Fig. 9 The DSC thermogram of 79.

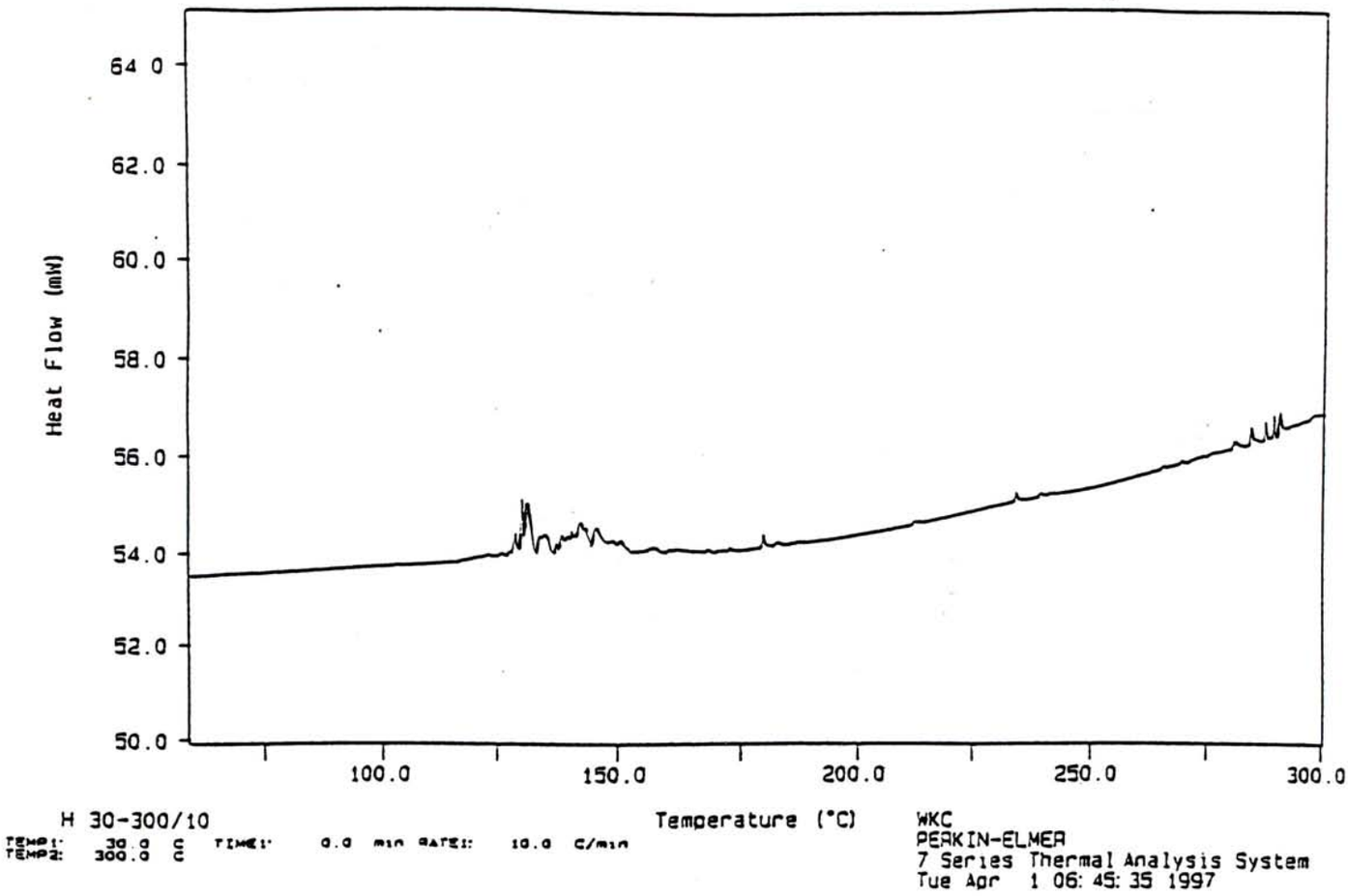


Fig. 10 DSC thermogram of 80.

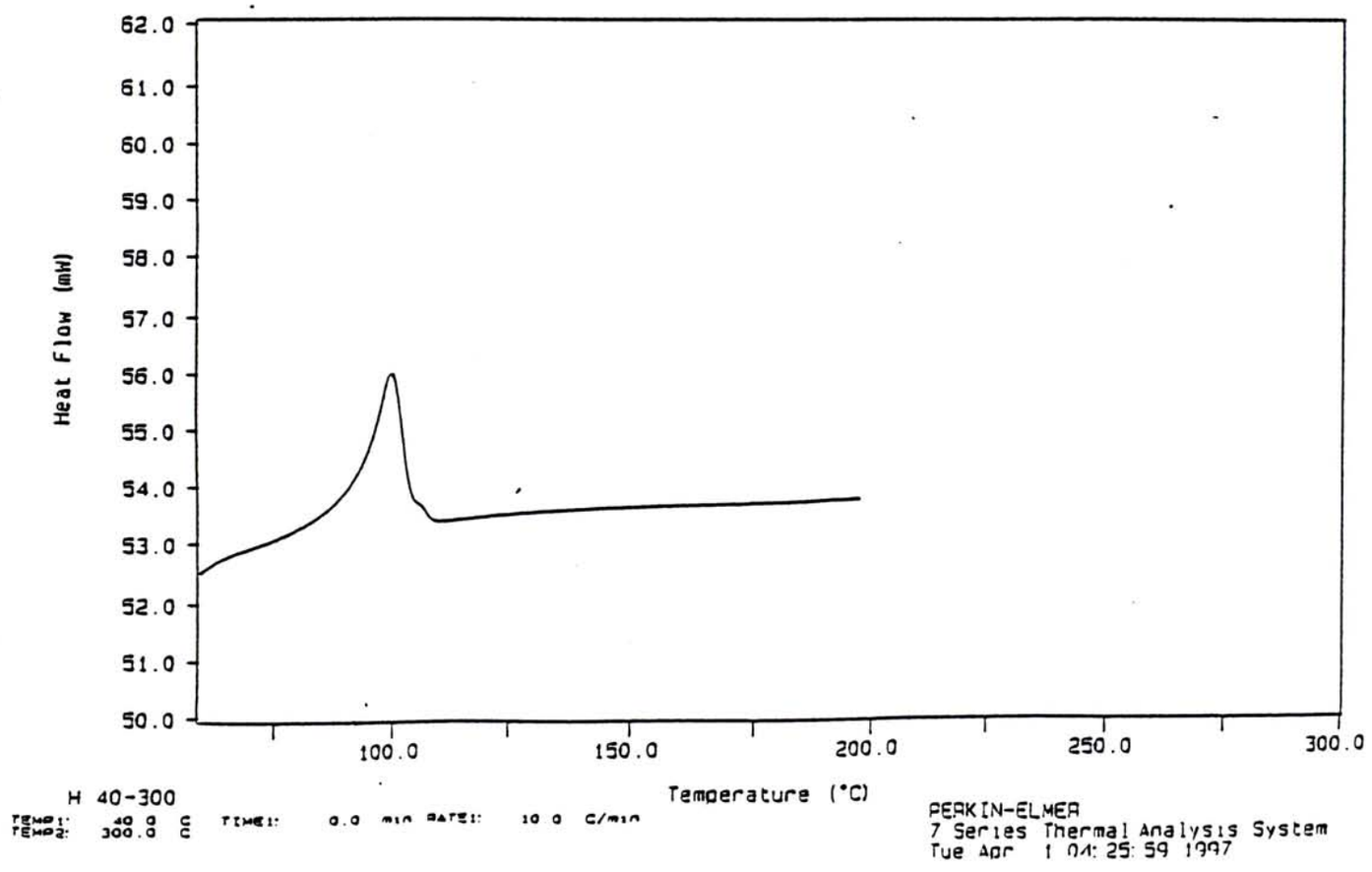


Fig. 11 DSC thermogram of 83.

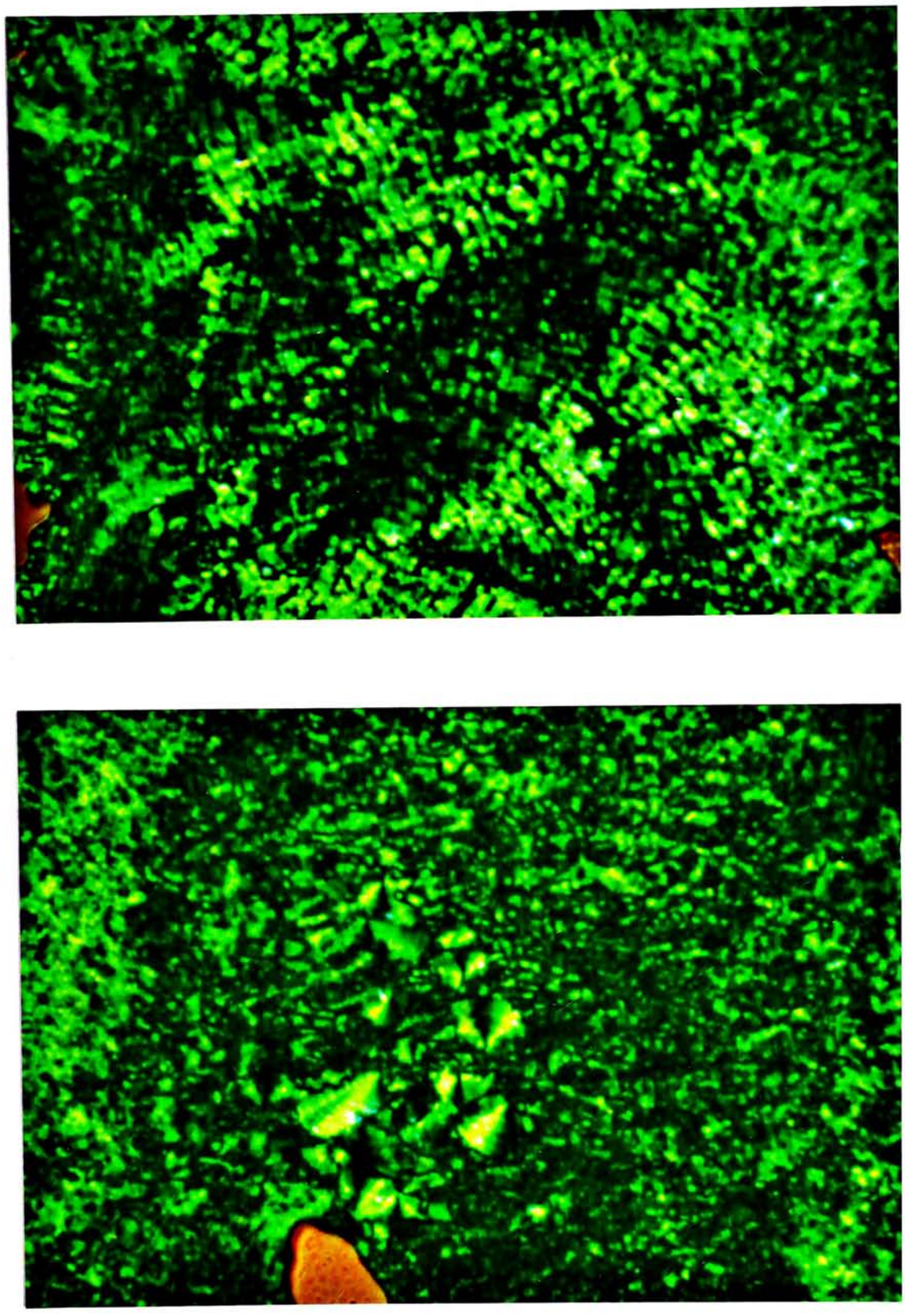


Fig. 12 Optical texture of **80** observed through a polarized mircoscope (140°C, 400 magnification).

2.3 Conclusions

A series of differently substituted Nc have been synthesized and spectroscopy characterized. The synthetic routes are rather general and it can be envisaged that special functionalities can be introduced readily by using these methods. These macrocycles having a large π-system tend to form molecular aggregates and this behavior has been studied with ^{1}H NMR and UV-Vis spectroscopy. Molecules with larger substituents have a lower aggregation tendency.

The first examples of columnar (molecule stack to each other and form many columns) liquid crystals based on a 2,3-Nc core have also been described. Because of the larger π-π stacking interactions, these liquid crystalline Ncs have higher clearing temperatures than the Pc analogs.

3. Experimental Section

3.1 Materials

Diethyl ether and THF were distilled from sodium benzophenone ketyl. Toluene, hexanes, *n*-pentanol and *n*-hexanol were distilled from sodium prior to use. DMF was dried over barium oxide and distilled under reduced pressure. Furan was shaken with 5% aqueous KOH, dried with Na_2SO_4, then distilled under nitrogen from sodium. Sodium methoxide was freshly prepared and *N*-bromosuccinimide was recrystallized from water. Butyl digol was distilled under reduced presure from sodium. Hexanes used in column chromatography was distilled from anhydrous $CaCl_2$. Column chromatographic purifications were carried out on silica gel column (Merck, Kieselgel 60, 70-230 mesh) with the indicated eluents. All other reagents and solvents were of reagent grade and used as received.

3.2 Physical Measurements

^1H and ^{13}C NMR spectra were recorded on a Bruker WM 250 (^1H, 250; ^{13}C, 62.9 MHz) or Bruker DPX 300 (^1H, 300; ^{13}C, 75.5 MHz) spectrometer in $CDCl_3$ solutions, unless stated otherwise, with a $SiMe_4$ internal standard ($\delta = 0$). Melting points were measured on a Electrothermal 9100 digital melting point apparatus and were uncorrected. The UV-Vis absorption spectra were obtained on a Hitachi U-3300

spectrometer. IR spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer or on a Nicolet Magna 550 spectrometer as KBr pellets. Electron Impact (EI) mass spectra were recorded on a VG 7070F (70eV) or HP 5989B spectrometer. Fast atom bombardment (FAB) and liquid secondary-ion (LSI) mass spectra were measured on a Bruker APEX 47e ultra-high resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with 3-nitrobenzyl alcohol as matrix. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry and the Microanalytical Department of the Inorganic Chemistry Laboratory, University of Oxford.

3.3 Preparation of (1,6,10,15,19,24,28,33-octamethyl-2,3-naphthalocyaninato)zinc(II) (**62**)

2,3,5,6-Tetrabromo-1,4-dimethylbenzene (41).[34] In a 250 mL three-necked round-bottomed flask connected with a condenser, catalytic amounts of iodine (1.3 g, 5 mmol) and iron powder (0.3 g, 5 mmol) were added to a solution of **39** (12.7 mL, 105 mmol) in CH_2Cl_2 (60 mL). Bromine (25.6 mL, 500 mmol) in CH_2Cl_2 (40 mL) was added dropwise over 6 h with stirring in dark. The reddish-brown solution was stirred overnight at 40°C. The resulting light purple suspension was poured into hexanes (500 mL) with stirring. The white precipitate was filtered off and washed with hexanes (50 mL). The crude product was recrystallized from toluene (2L) yielding white needles (33.2 g, 75%) which were dried at 50°C *in vacuo* overnight. ^{1}H NMR (250 MHz) δ 2.80 (s, $ArCH_3$); MS (EI): *m/z* 418 [M^+ based on ($^{79}Br)_4$, 17%].

6,7-Dibromo-1,4-epoxy-5,8-dimethyl-1,4-dihydronaphthalene (43).

Compound **41** (8.43 g, 20 mmol) and furan (10 mL, 138 mmol) in dry toluene (200 mL) was stirred at r.t. under nitrogen. A solution of 1.6 M *n*-BuLi (18.8 mL, 30 mmol) in dry toluene (200 mL) was added slowly over 3 h and the solution was stirred for a further 16 h at r.t.. Methanol (1 mL) was added, then the mixture was filtered and the filtrate was evaporated to give a pale yellow solid. Compound **43** was purified by column chromatography with hexanes / chloroform (1 : 1) as eluent (3.96 g, 60%). ^{1}H NMR (250 MHz) δ 7.03 (s, 2 H, C=CH), 5.78 (s, 2 H, C=CH), 2.40 (s, 6 H, $ArCH_3$); $^{13}C\{^1H\}$ NMR (62.9 MHz) δ 147.5, 142.6, 130.1, 124.8, 82.0, 20.8; MS (EI): *m/z* at 328 [M^+ based on $(^{79}Br)_2$, 18%]; Anal. Calcd. for $C_{12}H_{10}Br_2O$: C, 43.67; H, 3.05. Found: C, 44.27; H, 3.06.

2,3-Dibromo-1,4-dimethylnaphthalene (45). $TiCl_4$ (8.7 mL, 79 mmol) was added slowly to an ice-cold suspension of zinc dust (8.72 g, 133 mmol) in THF (100 mL). The mixture was refluxed for 10 min then cooled in an ice-bath. A solution of 6,7-dibromo-1,4-epoxy-5,8-dimethyl-1,4-dihydronaphthalene (**43**) (4.76 g, 14 mmol) in THF (50 mL) was then added in dropwise. The resulting mixture was refluxed overnight, cooled and then poured into cold HCl (10%, 250 mL). The mixture was extracted with CH_2Cl_2 (3 x 150 mL) and the combined extracts were washed with water (3 x 100 mL), dried over $CaCl_2$, and evaporated. The product was purified by column chromatography with hexanes as eluent (3.80 g, 84%). M.p. 156-160°C; ^{1}H NMR (250 MHz) δ 8.03-8.07 (m, 2 H, ArH), 7.52-7.57 (m, 2 H, ArH), 2.91 (s, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (62.9 MHz) δ 134.2, 131.9, 126.6, 125.6, 125.3, 21.3; MS (EI): *m/z* 312 [M^+ based on $(^{79}Br)_2$, 35%]; Anal. Calcd. for $C_{12}H_{10}Br_2$: C, 45.90; H, 3.21. Found: C, 46.16; H, 3.19.

2,3-Dicyano-1,4-dimethylnaphthalene (47). A mixture of **45** (2.20 g, 7.0 mmol) and CuCN (1.88 g, 21.0 mmol) in DMF was refluxed under nitrogen for 10 h. The mixture was cooled then poured into ammonia solution (35%, 100 mL) to which air was bubbled for 12 h. The solid residue was collected and extracted with $CHCl_3$ (3 x 250 mL). The combined organic extracts were washed with dilute NaCl solution (300 mL) and dried over $MgSO_4$. The volatiles were removed under reduced pressure to give a residue which was purified by column chromatography with CH_2Cl_2 as eluent (0.53 g, 37%). M.p. 243-247°C; ^{1}H NMR (250 MHz) δ 8.13-8.18 (m, 2 H, ArH), 7.79-7.85 (m, 2 H, ArH), 2.96 (s, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (62.9 MHz) δ 141.9, 132.7, 130.1, 125.9, 116.2, 109.9, 18.1; MS (EI): *m/z* 206 (M^+, 100%); IR: 3076w, 2988w, 2927w, 2222s ($\nu_{C\equiv N}$), 1438m, 1397s, 1196w, 1167w, 1019w, 940w, 869w, 769s, 638w, 599w, 520w cm^{-1}; Anal. Calcd. for $C_{14}H_{10}N_2$: C, 81.53; H, 4.89; N, 13.58. Found: C, 80.88; H, 4.80; N, 13.72.

(1,6,10,15,19,24,28,33-Octamethyl-2,3-naphthalocyaninato)zinc(II) (62). To a mixture of dinitrile **47** (152 mg, 0.74 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (55 mg, 0.25 mmol) in 1-hexanol (10 mL) at 90°C was added DBU (0.4 mL). The mixture was refluxed under nitrogen for 20 h then poured into a mixture of methanol / acetone (1 :1, 50 mL). The precipitate was washed with water, acetone and methanol, then dried *in vacuo* (90 mg, 55%). The green powder was then Soxhlet extracted with methanol / acetone (1 : 1) followed by THF. UV-Vis (THF, λmax nm): 331, 412, 708, 753, 791; IR: 3073w, 2924m, 2858w, 1705w, 1651w, 1609m, 1521m, 1476m, 1407m, 1381m, 1358m, 1407m, 1328m, 1196m, 1127s, 1014s, 940w, 822w, 751s cm^{-1}; Anal. Calcd. for

$C_{56}H_{40}N_8Zn$ (**65**·$2CH_3OH$): C, 72.99; H, 5.07; N, 11.74. Found: C, 72.55; H, 5.04; N, 11.63.

3.4 Preparation of (1,6,10,15,19,24,28,33-octahexyl-2,3-naphthalocyaninato)zinc(II) (**63**)

1,4-Dihexylbenzene (**40**).[36] The Grignard reagent prapared from Mg turnings (3 g, 0.3 mol) and hexyl bromide (42.2 mL, 0.3 mol) in dry Et_2O (150 mL) was added in dropwise to a mixture of 1,4-dichlorobenzene (16.8 g, 0.11 mol) and dichloro[1,3-bis(diphenylphosphine)propane]nickel(II) (180 mg) in dry Et_2O (90 mL) in a 250 mL 3-necked round-bottomed flask at r.t.. When the reaction became vigorous, the flask was cooled in an ice-bath and the reaction mixture was stirred at this temp. for 12 h. The solution was then hydrolysed with HCl (2M). The organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with H_2O (3 x 40 mL), $NaHCO_3$ (5%, 3 x 40 mL) and H_2O (3 x 40 mL), then dried over anhydrous $CaCl_2$. After removal of volatiles, the residue was dissolved in hexane (100ml) and passed through a short bed of silica gel. The solvent was removed to give **40** (15.1 g, 53%) as a colorless liquid. ^{1}H NMR (250 MHz) δ 7.11 (s, 4 H, ArH), 2.56 (t, J = 7.7 Hz, 4 H, ArH), 1.59 (m, 6 H, CH_2), 1.30 (m, 10 H, CH_2), 0.88 (t, J = 6.5 Hz, 6 H, CH_3).

2,3,5,6-Tetrabromo-1,4-dihexylbenzene (**42**). Iodine (0.12 g, 1 mmol) and iron powder (0.054 g, 1 mmol) were added to the mixture of 1,4-dihexylbenzene (**40**) (6.0 g,

24 mmol) and CH_2Cl_2 (10 mL) in a 100ml 3-necked round-bottomed flask. Bromine (5.1 mL, 10 mmol) was added in dropwise into the mixture over 3 h. The whole setup was covered with an aluminium foil. When the addition of bromine was completed, the mixture was heated at 40°C overnight. The brown mixture was then poured into $NaHSO_3$ (5%, 500 mL) and the yellow organic layer was separated, washed with H_2O (3 x 50 mL) and dried over Na_2SO_4. After removal of solvent, the crude product was recrystallized from hexane to yield **42** (11.5 g, 84%) as colorless needle-shaped crystals. M.p. 181.2-182.3°C; ^{1}H NMR (250 MHz) δ 3.16 (t, J = 7.8 Hz, 4 H, CH_2), 1.33-1.57 (m, 16 H, CH_2), 0.91 (t, J = 6.6 Hz, 6 H, CH_3); MS (EI): *m/z* 558 [M^+ based on $(^{79}Br)_4$, 16%]; Anal. Calcd. for $C_{18}H_{26}Br_4$: C, 38.47; H, 4.66. Found: C, 38.66; H, 4.41.

6,7-Dibromo-1,4-epoxy-5,8-dihexyl-1,4-dihydronaphthalene (44). Compound **36** (5.00 g, 9 mmol) and furan (4.5 mL, 62 mmol) in dry hexanes (200 mL) was stirred at r.t. under nitrogen. Then a solution of n-BuLi (1.6 M in hexanes, 8.3 mL, 13 mmol) in hexane (200 mL) was added dropwise over 3 h and the mixture was stirred for a further 16 h at r.t.. Methanol (1 mL) was added, then the mixture was filtered and the filtrate was evaporated under reduced pressure to give **44** as a pale yellow oil which crystallized in hexanes as white crystals (1.50 g, 36%). M.p. 68-70°C; ^{1}H NMR (250 MHz) δ 7.02 (s, 2 H, C=CH), 5.75 (s, 2 H, OCH), 2.81 (vt, J = 7.7 Hz, 4 H, $ArCH_2$), 1.45-1.58 (m, 4 H, CH_2), 1.32-1.37 (m, 12 H, CH_2), 0.90, (vt, J = 6.3 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (125.8 MHz) δ 147.5, 142.7, 134.9, 124.5, 81.8, 34.8, 31.6, 29.8, 29.3, 22.6, 14.0; MS (EI): an isotopic cluster peaking at *m/z* 468 [M^+ based on $(^{79}Br)_2$, 6%]; Anal. Calcd. for $C_{22}H_{30}Br_2O$: C, 56.19; H, 6.43. Found: C, 55.99; H, 6.48.

2,3-Dibromo-1,4-dihexylnaphthalene (46). $TiCl_4$ (3.7 mL, 33.4 mmol) was added slowly to an ice-cold suspension of zinc dust (3.7 g, 56.6 mmol) in THF (100 mL). The mixture was refluxed for 10 min then cooled in an ice-bath. A solution of compound **44** (2.9 g, 6.2 mmol) in THF (40 mL) was then added in dropwise. The resulting mixture was refluxed overnight, cooled, and then poured into cold HCl (10%, 200 mL). The mixture was extracted with CH_2Cl_2 (3 x 100 mL) and the combined organic portions were washed with water (3 x 100 mL), dried over $CaCl_2$ and evaporated. The crude product was chromatographed with ethyl acetate / hexanes (1 : 10) as eluent, then recrystallized from hexanes giving white crystals (2.4 g, 84%). M.p. 57-58°C; ^{1}H NMR (250 MHz) δ 8.02-8.06 (m, 2 H, ArH), 7.52-7.56 (m, 2 H, ArH), 3.33 (vt, J = 8.1 Hz, 4 H, $ArCH_2$), 1.46-1.70 (m, 8 H, CH_2), 1.35-1.40 (m, 8 H, CH_2), 0.92 (vt, J = 7.0 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (125.8 MHz) δ 139.0, 131.7, 126.5, 125.4, 125.2, 34.9, 31.6 29.7, 29.4, 22.7, 14.1; MS (EI): an isotopic cluster peaking at *m/z* 452 [M^+ based on $(^{79}Br)_2$, 55%]; Anal. Calcd. for $C_{22}H_{30}Br_2$: C, 58.17; H, 6.66. Found: C, 58.39; H, 6.67.

2,3-Dicyano-1,4-dihexylnaphthalene (33). Compound **46** (1.2 g, 2.6 mmol) and CuCN (0.7 g, 7.8 mmol) were dissolved in DMF (15 mL) and the mixture was heated at 170°C for 10 h under nitrogen. An 35% ammonia solution (40 mL) was added and the mixture was bubbled with air overnight. The precipitate was filtered off and washed with $CHCl_3$ (3 x 20 mL) and the filtrate was extracted with $CHCl_3$ (3 x 50 mL). The combined organic portions were evaporated to give a solid which was recrystallized from hexanes to give pale yellow needles (0.4 g, 44%). M.p. 95-96°C; ^{1}H NMR (250MHz) δ 8.15-8.19 (m, 2 H, ArH), 7.76-7.80 (m, 2 H, ArH), 3.33 (vt, J = 8.0 Hz, 4

H, $ArCH_2$), 1.68-1.77 (m, 4 H, CH_2), 148-1.55 (m, 4 H, CH_2), 1.32-1.38 (m, 8 H, CH_2), 0.89 (vt, J = 7.0 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (125.8MHz) δ 146.7, 132.5, 129.8, 125.9, 116.2, 109.8, 32.1, 31.5, 31.0, 29.5, 22.5, 14.0; MS (EI): *m/z* 346 (M^+, 100%); Anal. Calcd. for $C_{24}H_{30}N_2$: C, 83.19; H, 8.73; N, 8.08. Found: C, 83.05; H, 8.99; N, 8.31.

(1,6,10,15,19,24,28,33-Octahexyl-2,3-naphthalocyaninato)zinc(II) (63). By using the procedure described for **62**, compound **33** (260 mg, 0.75 mmol) was treated with $Zn(OAc)_2 2H_2O$ (55 mg, 0.25 mmol) and DBU (0.4 mL) in refluxing 1-hexanol (10 mL) for 20 h. The crude product was subjected to chromatography with hexanes / ethyl acetate (9 : 1) as eluent giving a brown powder (45 mg, 17%). ^1H NMR (250 MHz) δ 8.70-8.80 (m, 8 H, ArH), 7.80-7.89 (m, 8 H, ArH), 5.04-5.27 (m, 16 H, $ArCH_2$), 1.94-2.11 (m, 16 H, CH_2), 1.61-1.77 (m, 16 H, CH_2), 1.12-1.35 (m, 16 H, CH_2), 0.85 (quintet, J = 7.0 Hz, 16 H, CH_2), 0.71 (t, J = 7.0 Hz, 24 H, CH_3); UV-Vis [THF, λmax nm (log ε)]: 722 (4.67), 808 (5.30); MS (LSI): an isotopic cluster peaking at *m/z* 1450.90 [Calcd. for MH^+ 1450.89]; IR: 3074w, 2954s, 2924s, 2853s, 1707m, 1649m, 1598m, 1462m, 1356m, 1133m, 1093m, 754m, 727w cm^{-1}.

3.5 Preparation of (2,5,11,14,20,23,29,32-octahexyl-1,6,10,15,19,24,28,33-octamethyl-2,3-naphthalocyaninato)zinc(II) (**67**)

2-hexylfuran (49).[31] Furan (2.1 mL, 30 mmol) was added in dropwise into a stirred solution of *n*-BuLi (20 mL, 30 mmol) and dry THF (13 mL) under N_2 at -15°C to

give a yellow solution. The mixture was then stirred for 24h at r.t. to give an orange-red solution. Hexylbromide (4.2 mL, 30 mmol) was then added in dropwise to the solution and the mixture was stirred at r.t. for 24 h. The red solution was then poured into ice and extracted with Et_2O (3 x 100 mL). The organic extracts were combined and dried over $MgSO_4$. The solvent was removed in vacuum, then the crude product was dissolved in hexane and passed through a short bed of silica gel. After removal of solvent, **49** (3.8 g, 85%) was obtained as a pale yellow liquid. ^1H NMR (250 MHz) δ 7.31 (t, J = 0.9 Hz, 1 H, C=CH), 6.29 (t, J = 2.4 Hz, 1 H, C=CH), 5.98 (m, 1 H, C=CH), 2.63 (t, J = 7.6 Hz, 1 H, CH_2), 1.68-1.32 (m, 8 H, CH_2), 0.92 (m, 3 H, CH_3).

2,5-Dihexylfuran (50).[31] 2-Hexylfuran (**49**) (3.8 g, 24 mmol) was added in dropwise into a stirred solution of *n*-BuLi (15 mL, 23 mmol) in dry THF (10 mL) under N_2 at -15°C to give a yellow solution. The mixture was then stirred for 24 h at r.t. to give a red solution. Hexylbromide (4.2 mL, 30 mmol) was added in dropwise to the solution and the mixture was stirred at r.t. for 24 h. The deep-red solution was then poured into ice and extracted with Et_2O (3 x 100 mL). The organic extracts were separated and dried over $MgSO_4$. The volatiles were removed in vacuum, then the crude product was dissolved in hexane and passed through a short bed of silica gel. After removal of volatiles,, **50** (3.4 g) (crude product) was obtained as a yellow liquid. Further purification by chromatography give **50** (3.3 g, 58%) as a colourless liquid. ^1H NMR (250 MHz) δ 5.83 (s, 2 H, C=CH), 2.56 (t, J = 7.6 Hz, 4 H, CH_2), 1.85-1.30 (m, 8 H, CH_2), 0.9 (t, J = 6.5 Hz, 6 H, CH_3).

6,7-Dibromo-1,4-epoxy-1,4-dihexyl-5,8-dimethyl-1,4-dihydronaphthlene (51). Compound **41** (8.43 g, 20 mmol) and 2,5-dihexylfuran (**50**) (6.86 g, 29 mmol) in

dry toluene (200 mL) was stirred at r.t. under nitrogen. Then a solution of *n*-BuLi (1.6 M in hexanes, 18.8 mL, 30 mmol) in dry toluene (200 mL) was added in dropwise over 3 h and the mixture was stirred for a further 16 h at r.t.. Methanol (1 mL) was added, the mixture was filtered and the filtrate was evaporated under reduced pressure. Compound **51** was purified by column chromatography with hexanes / chloroform (4 : 1) as eluent to give a colourless liquid (4.98 g, 50%). ^{1}H NMR (250 MHz) δ 6.71 (s, 2 H, C=CH), 2.46 (s, 6 H, CH_3), 2.31-2.36 (m, 4 H, $ArCH_2$), 1.31-1.59 (m, 16 H, CH_2), 0.89 (vt, J = 6.5 Hz, 6 H, CH_3); ^{13}C{^{1}H} NMR (62.9 MHz) δ 150.5, 146.1, 129.8, 126.2, 93.0, 32.1, 31.7, 29.7, 25.0, 22.6, 20.4, 14.0; HRMS (LSI) *m/z* calcd. for $C_{24}H_{35}{}^{79}Br_2O$ (MH^+): 497.1056, found: 497.1164.

2,3-Dibromo-5,8-dihexyl-1,4-dimethylnaphthalene (53). $TiCl_4$ (2.0 mL, 18.2 mmol) was added carefully to an ice-cold suspension of zinc dust (2.0 g, 30.6 mmol) in THF (100 mL). The mixture was refluxed for 10 min then cooled in an ice-bath. A solution of compound **51** (1.6 g, 3.3 mmol) in THF (40 mL) was then added in dropwise. The resulting mixture was refluxed for 15 h, cooled and then poured into cold HCl (10%, 200 mL). The mixture was extracted with CH_2Cl_2 (3 x 100 mL) and the combined organic portions were washed with water (3 x 100 mL), dried over $CaCl_2$, and evaporated to give a colourless liquid. Compound **53** was purified by column chromatography with hexanes as eluent (1.1 g, 70%). ^{1}H NMR (250 MHz) δ 7.20 (s, 2 H, ArH), 2.96 (vt, J = 8.0 Hz, 4 H, $ArCH_2$), 2.81 (s, 6 H, CH_3), 1.47-1.63 (m, 4 H, CH_2), 1.16-1.35 (m, 12 H, CH_2), 0.86 (vt, J = 6.8 Hz, 6 H, CH3); ^{13}C{^{1}H} NMR (62.9 MHz) δ 137.8, 135.5, 134.1, 127.8, 126.5, 36.9, 32.1, 31.6, 29.5, 27.0, 22.6, 14.0; MS (EI): an

isotopic cluster peaking at m/z 480 [M^+ based on ($^{79}Br)_2$, 8%]; HRMS (LSI) *m/z* calcd. for $C_{24}H_{34}{}^{79}Br_2$ (M^+): 480.1028, found: 480.0991.

2,3-Dicyano-5,8-dihexyl-1,4-dimethylnaphthalene (55). Compound **53** (1.35 g, 2.8 mmol) was mixed with CuCN (0.75 g, 8.4 mmol) in DMF (10 mL) under nitrogen. The light green suspension was refluxed for 6 h then cooled to r.t.. An 35% ammonia solution (40 mL) was added to the mixture and air-bubbled overnight. The suspension was filtered and the filtrate was extracted with chloroform (3 x 50 mL), dried over $CaCl_2$, and rotary evaporated. The crude product was purified by column chromatography with hexanes as eluent yielding a white solid (0.73 g, 70%). M.p. 50-51°C; ^{1}H NMR (250MHz) δ 7.46 (s, 2 H, ArH), 3.14 (vt, J = 7.9 Hz, 4 H, $ArCH_2$), 3.01 (s, 6 H, CH_3), 1.50-1.65 (m, 4 H, CH_2), 1.19-1.43 (m, 12 H, CH_2), 0.90 (vt, J = 6.5 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (62.9 MHz) δ 142.0, 140.1, 135.7, 132.0, 116.6, 110.8, 37.1, 32.4, 31.5, 29.3, 23.3, 22.5, 13.9; MS (EI): *m/z* 374 (M^+, 100%); IR: 2956s, 2922s, 2856s, 2222s ($\nu_{C\equiv N}$), 1578w, 1461m, 1378m, 1178w, 1128w, 1033w, 944w, 844w, 800w, 722w, 667w, 522w cm^{-1}; Anal. Calcd. for $C_{26}H_{34}N_2$: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.46; H, 9.21; N, 7.39.

(2,5,11,14,20,23,29,32-Octahexyl-1,6,10,15,19,24,28,33-octamethyl-2,3-naphthalocyaninato)zinc(II) (67). Compound **55** (220 mg, 0.59 mmol) was treated with $Zn(OAc)_2{\cdot}2H_2O$ (40 mg, 0.18 mmol) and DBU (0.4 mL) in refluxing 1-hexanol (10 mL) for 16 h. The crude product was purified by column chromatography with hexanes / ethyl acetate (5 : 1) as eluent (40 mg, 17%). UV-Vis [hexane, λmax nm (log ε)]: 727 (4.75), 812 (5.35); MS (LSI): an isotopic cluster peaking at *m/z* 1562.92 [Calcd. for MH^+ 1563.01].

3.6 Preparation of (2,5,11,14,20,23,29,32-octahexyl-2,3-naphthalocyaninato)zinc(II) (**64**)

6,7-Dibromo-1,4-epoxy-1,4-dihexyl-1,4-dihydronaphthalene (52). A mixture of tetrabromobezene **48** (6.00 g, 15 mmol) and 2,5-dihexylfuran (**50**) (3.88 g, 16 mmol) in toluene (250 mL) was stirred at r.t. under nitrogen, then a solution of *n*-BuLi (1.6 M in hexanes, 15 mL, 24 mmol) in toluene (100 mL) was added in dropwise over 3 h. The mixture was stirred for a further 16 h at r.t., then methanol (1 mL) was added. The mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was subjected to column chromatography with hexanes / chloroform (5 : 1) as eluent giving a pale yellow oil (3.36 g, 48%). ^{1}H NMR (250 MHz) δ 7.30 (s 2 H, ArH), 6.73 (s, 2 H, C=CH), 2.12-2.20 (m, 4 H, $ArCH_2$), 1.50-1.68 (m, 4 H, CH_2), 1.28-1.50 (m, 12 H, CH_2), 0.86-1.00 (m, 6 H, CH_3); $^{13}C\{^{1}H\}$ NMR (125.8 MHz) δ 154.1, 145.5, 124.1, 120.2, 91.7, 31.7, 29.7, 29.2, 24.6, 22.6, 14.1; MS (EI): *m/z* 468 [M^+ based on $(^{79}Br)_2$, 22%].

2,3-Dibromo-5,8-dihexylnaphthalene (54). To an ice-cold suspension of zinc dust (4.7 g, 71 mmol) in THF (120 mL) was added slowly $TiCl_4$ (5.2 mL, 47 mmol) under nitrogen. The mixture was refluxed for 10 min then cooled in an ice-bath. A solution of **52** (3.4 g, 7 mmol) in THF (50 mL) was then added in dropwise. The mixture was refluxed overnight, cooled and then poured into cold 10% HCl (250 mL). The mixture was extracted with CH_2Cl_2 (3 x 100 mL) and the combined extracts were

washed with water (3 x 50 mL), dried over $CaCl_2$, and evaporated. The residue was purified by chromatography with hexanes as eluent to yield a pale yellow oil which crystallized in hexanes as white crystals (2.5 g, 76%). M.p. 48-49°C; ^{1}H NMR (250 MHz) δ 8.29 (s, 2 H, ArH), 7.24 (s, 2 H, ArH), 2.94 (vt, J = 7.8 Hz, 4 H, $ArCH_2$), 1.63-1.72 (m, 4 H, CH_2), 1.30-1.44 (m, 12 H, CH_2), 0.89 (vt, J = 6.9 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ (125.8 MHz) δ136.34, 132.3, 129.4, 126.8, 121.4, 32.7, 31.7, 30.6, 29.3, 22.6, 14.1; MS (EI): *m/z* 452 [M^+ based on $(^{79}Br)_2$, 50%]; Anal. Calcd. for $C_{22}H_{30}Br_2$: C, 58.17; H, 6.66. Found: C, 58.37; H, 6.83.

2,3-Dicyano-5,8-dihexylnaphthalene (56). Compound **54** (1.10 g, 2.4 mmol) and CuCN (0.65 g, 7.3 mmol) were dissolved in DMF (10 mL) and the mixture was heated at 140°C for 10 h under nitrogen. An 35% ammonia solution (40 mL) was added to the mixture to which air was bubbled overnight. The precipitate was filtered off and washed with $CHCl_3$ (3 x 20 mL). The filtrate was extracted with $CHCl_3$ (3 x 50 mL) and the combined organic portions were dried over $MgSO_4$ and evaporated *in vacuo*. The crude product was recrystallized from hexanes to give pale yellow needles (0.40 g, 48%). M.p.85-87°C; ^{1}H NMR (250 MHz) δ 8.52 (s, 2 H, ArH), 7.52 (s, 2 H, ArH), 3.03 (vt, J = 7.8 Hz, 4 H, $ArCH_2$), 1.61-1.75 (m, 4 H, CH_2), 1.29-1.50 (m, 12 H, CH_2), 0.89 (vt, J = 6.9 Hz, CH_3); $^{13}C\{^1H\}$ NMR (125.8 MHz) δ 138.5, 132.8, 132.5, 130.6, 116.4, 109.1, 32.6, 31.6, 31.0, 29.3, 22.6, 14.0; MS (EI): *m/z* at 346 (M^+, 14%); Anal. Calcd. for $C_{24}H_{30}N_2$: C, 83.19; H, 8.73; N, 8.08. Found; C, 83.81; H, 8.92; N, 8.25.

(2,5,11,14,20,23,29,32-Octahexyl-2,3-naphthalocyaninato)zinc(II) (64). A mixture of compound **56** (250 mg, 0.72 mmol) and $Zn(OAc)_2 2H_2O$ (50 mg, 0.23 mmol) in 1-hexanol (10 mL) was heated at 90°C, then DBU (0.4 mL) was added and the

mixture was refluxed under nitrogen for 3 h. The mixture was cooled then poured into methanol / water (1 : 1, 50 mL). The precipitate was filtered off and the filtrate was mixed with methanol (50 mL) to give a second crop of green solid. The combined solid was dissolved into hexanes (50 mL) then subjected to chromatography with hexanes / THF (2 : 1) as eluent giving a green powder which was recrystallized from hexanes (124 mg, 47%). ^{1}H NMR (250 MHz, THF-d_8, 2.8 x 10^{-3} M) δ 9.60 (br s, 8 H, ArH), 7.44 (br s, 8 H, ArH), 3.52 (br s, 16 H, $ArCH_2$), 2.10-2.22 (m, 16 H, CH2), 1.80-1.92 (m, 16 H, CH_2), 1.43-1.66 (m, 32 H, CH_2), 1.05 (t, J = 6.9 Hz, 24 H, CH_3); UV-Vis [THF, λmax nm (log ε)]: 338 (4.82), 684 (4.55), 729 (4.60), 766 (5.34); MS (LSI): an isotopic cluster peaking at *m/z* 1451.09 [Calcd. for MH^+ 1450.89]; IR: 2922s, 2852m, 1654w, 1579w, 1463m, 1370s, 1120s, 731w cm-1; Anal. Calcd. for $C_{96}H_{120}N_8Zn$: C, 79.44; H, 8.33; N, 7.72. Found: C, 78.68; H, 8.38; N, 7.55.

3.7 Preparation of (3,4,12,13,21,22,30,31-octapropylthio-2,3-naphthalocyaninato)zinc(II) (**65**)

4,5-Dibromo-1,2-dimethylbenzene (**57**).[39] *O*-xylene (46 mL, 0.35 mol) and iodine (0.2 g) were mixed in a 250 mL two-necked round-bottomed flask. Bromine (40 mL, 1.3 mol) was then added in dropwise in 2 h at 0°C and the resulting mixture was stirred for 12 h at r.t.. Diethyl ether (150 mL) was added to dissolve the solid and the solution was washed with 2N NaOH (3 x 50 mL) and brine (3 x 50 mL), then dried over $MgSO_4$. The solvent was evaporated and the solid obtained was recrystallized from

methanol to give **57** as white crystals (53 g, 53%). M.p. 86-88°C; ^{1}H NMR (250 MHz) δ 7.36 (s, 2 H, ArH), 2.18 (s, 6 H, CH_3).

4,5-Dibromo-1,2-bis(dibromomethyl)benzene (58).[40] Compound **57** (8.0 g, 30 mmol), NBS (11 g, 60 mmol) and dibenzoyl peroxide (0.32 g, 1.3 mmol) were added in CCl_4 (150 mL) in a 250 mL round-bottomed flask fitted with a $CaCl_2$ drying tube. The reaction mixture was refluxed for 5 h, then a second portion of NBS (11 g, 60 mmol) was added. After refluxing the reaction mixture for a further 12 h, a third portion of NBS (11 g, 60 mmol) was added, and the suspension was refluxed for a further 7 h. The reaction mixture was then cooled, filtered, and the filtrate was concentrated. The crude product was dissolved in hot $CHCl_3$ and hexanes was added to precipitate compound **58** out as yellow powder (11.0 g, 64%). M.p. 128-129°C; ^{1}H NMR (250 MHz) δ 7.92 (s, 2 H, ArH), 6.97 (s, 2 H, $ArCBr_2H$).

6,7-Dibromo-2,3-dicyanonaphthalene (11).[28] Compound **58** (10 g, 18 mmol), furmaronitrile (1.5 g, 19 mmol) and anhydrous sodium iodide (20 g, 130 mmol) were added into DMF (140 mL) in a 150 mL round-bottomed flask fitted with a $CaCl_2$ drying tube. The brown mixture was stirred at 75°C for 7 h. The dark brown reaction mixture was then cooled and poured carefully into water (300 mL) with stirring. Sodium metasulphate was added to the aqeuous mixture until the colour changed to pale yellow. The pale yellow solid was collected, washed with hot EtOAc, then dried under reduced pressure overnight (3.3 g, 54%). M.p. 248-249°C; ^{1}H NMR (250 MHz) δ 8.30 (s, 2 H, ArH), 8.26 (s, 2 H, ArH); I.R.: 3055w, 2923w, 2852w, 2233s ($\nu_{C\equiv N}$), 1686w, 1571m, 1427s, 1381m, 1346m, 1099s, 945s, 923s cm^{-1}.

ArH), 8.26 (s, 2 H, ArH); I.R.: 3055w, 2923w, 2852w, 2233s ($\nu_{C\equiv N}$), 1686w, 1571m, 1427s, 1381m, 1346m, 1099s, 945s, 923s cm^{-1}.

2,3-Dicyano-6,7-dipropylthionaphthalene (61). To an ice-cold suspension of NaH (60 % dispersion in mineral oil, 0.08 g, 2.0 mmol) in DMF (30 mL) was added slowly 1-propanethiol (0.19 mL, 2.1 mmol). The mixture was stirred for a few min until the evolution of hydrogen gas was completed, then 2,3-dibromo-6,7-dicyanonaphthalene (**11**) (0.34 g, 1.0 mmol) and copper(I) oxide (0.28 g, 2.0 mmol) were added and the mixture was refluxed for 3 h. The cooled mixture was poured into ice then extracted with Et_2O (3 x 50 mL). The combined organic portions were washed with ammonia solution (35%, 3 x 30 mL) and water (3 x 30 mL), then dried over K_2CO_3. The solution was rotary-evaporated to give a yellow solid which was essentially pure for further reactions (0.29 g, 89%). Analytically pure sample was obtained by recrystallization from a $CHCl_3$ / hexanes mixture. M.p. 196-197°C; ^1H NMR (250MHz) δ 8.15 (s, 2 H, ArH), 7.58 (s, 2 H, ArH), 3.07 (t, J = 7.3 Hz, 4 H, SCH_2), 1.83 (sextet, J = 7.3 Hz, 4 H, CH_2), 1.12 (t, J = 7.3 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (62.9MHz) δ 142.7, 134.0, 130.8, 123.2, 116.1, 109.3, 34.9, 21.6, 13.7; MS (EI): *m/z* 326 (M^+, 58%); IR: 2962s, 2929s, 2872s, 2220m ($\nu_{C\equiv N}$), 1463m, 1424s, 1386m, 1230m, 1105m, 908m, 750m, 590m cm^{-1}; Anal. Calcd. for $C_{18}H_{18}N_2S_2$: C, 66.22; H, 5.56; N, 8.58; S, 19.64. Found: C, 65.63; H, 5.55; N, 8.46; S, 19.42.

(3,4,12,13,21,22,30,31-Octapropylthio-2,3-naphthalocyaninato)zinc(II) (65). Dinitrile **61** (250 mg, 0.77 mmol) was treated with $Zn(OAc)_2.2H_2O$ (53 mg, 0.24 mmol) and DBU (0.4 mL) in refluxing 1-hexanol (10 mL) for 5 h. The cooled solution was poured into methanol / water (1 : 1, 50 mL) and the precipitate formed was filtered off

25 mg of a deep green solid while most of the material stuck in the column. Alternatively, the green solid was Soxhlet extracted with methanol / acetone (1 : 1) for two days. The extract was discarded and the solid was further extracted with $CHCl_3$. After evaporating the $CHCl_3$ extract, analytically pure **65** was obtained. UV-Vis [THF, 1.94 x 10^{-7} M, λmax nm (log ε)]: 355 (4.83), 693 (4.41), 745 (4.59), 778 (5.17); MS (LSI): an isotopic cluster peaking at *m/z* 1370.22 [Calcd. for MH^+ 1370.30]; IR: 2961m, 2928m, 2871w, 1722w, 1626w, 1582m, 1455s, 1410m, 1345m, 1261w, 1144w, 1103s, 1033s, 904w, 803w, 736w, 696w cm^{-1}; Anal.Calcd. for $C_{74}H_{74}Cl_6N_8S_8Zn$ (**65**·2$CHCl_3$): C, 55.20; H, 4.63; N, 6.96. Found: C, 54.91; H, 5.03; N, 6.63.

3.8 Preparation of (3,4,12,13,21,22,30,31-octaphenylthio-2,3-naphthalocyaninato)zinc(II) (**66**)

2,3-Dicyano-6,7-diphenylthionaphthalene (13).[30] By using the procedure described for **61** with thiophenol (0.22 mL, 2.1 mmol) as the starting material and refluxing the mixture overnight, compound **13** was obtained which was purified by column chromatography with hexanes / chloroform (1 : 1) as eluent (0.33 g, 84%). M.p. 246-247°C (lit. 256-257°C)[29]; ^{1}H NMR (250 MHz) δ 7.95 (s, 2 H, ArH), 7.53-7.59 (m, 4 H, Ph), 7.48-7.51 (m, 6 H, Ph), 7.28 (s, 2 H, ArH); $^{13}C\{^1H\}$ NMR (62.9 MHz) δ 142.8, 134.5, 134.4, 131.2, 130.6, 130.2, 129.7, 125.9, 115.8, 109.5; MS (EI): *m/z* 394 (M^+, 100%); IR: 3053w, 2912w, 2231s ($\nu_{C\equiv N}$), 1561m, 1425s, 1096m, 924m, 750s, 691m cm^-

[1]; Anal. Calcd. For $C_{24}H_{14}N_2S_2$: C, 73.07; H, 3.58; N, 7.10; S, 16.25. Found: C, 72.75; H, 3.39; N, 6.93; S, 16.37.

(3,4,12,13,21,22,30,31-Octaphenylthio-2,3-naphthalocyaninato)zinc(II) (66). By using the procedure described for compound **65**, dinitrile **13** (250 mg, 0.63 mmol) was converted to **66**, which was purified by column chromatography with THF as eluent (125 mg, 48%). Analytically pure sample was prepared by Soxhlet extraction with methanol / acetone (1 : 1) followed by $CHCl_3$. UV-Vis [THF, λmax nm (log ε)]: 353 (6.16), 694 (4.92), 741 (4.90), 779 (5.67); MS (LSI): an isotopic cluster peaking at *m/z* 1642.09 [Calcd. for MH^+ 1642.17]; IR: 3053w, 2912w, 2838w, 1579m, 1476m, 1439m, 1406m, 1370m, 1342s, 1088s, 1024m, 728m, 689m cm^{-1}; Anal. Calcd. for $C_{98}H_{58}Cl_6N_8S_8Zn$ (**66**·2$CHCl_3$): C, 62,54; H, 3.11; N, 5.95. Found: C, 62.74; H, 3.52; N, 5.67.

3.9 Preparation of (2,5,11,14,20,23,29,32-octahexyloxymethyl-2,3-naphthalocyaninato)zinc(II) (**79**)

6,7-Dibromo-1,4-dimethyl-1,4-epoxy-1,4-dihydronaphthalene (68). Compound **48** (8.0 g, 20 mmol) and 2,5-dimethylfuran (10 mL, 94 mmol) were stirred in dry toluene (250 mL) at r.t.. n-BuLi (15 mL, 24 mmol) in dry toluene (200 mL) was added dropwise over 3 h and stirred for another 16 h. MeOH (1 mL) was added, the solution was filtered and evaporated. After chromatography **68** (2.7 g, 41%) was obtained as a pale yellow solid. M.p. 98-100°C; ^{1}H NMR (250 MHz) δ 7.33 (s, 2 H, Ar-

H), 6.74 (s, 2 H, Ar-H), 1.86 (s, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (62.9 MHz) δ 154.51, 146.87, 124.26, 120.88, 88.88, 15.49; MS (EI): m/z 328 [M^+ based on $(^{79}Br)_2$, 20%]; Anal. Calcd. for $C_{12}H_{10}Br_2O$: C, 43.67; H, 3.05. Found: C, 43.42; H, 2.92.

2,3-Dibromo-5,8-dimethylnaphthalene (69). To an ice-cold suspension of Zn dust (5.9 g, 91 mmol) in dry THF (120 mL) was carefully added $TiCl_4$ (5.2 mL, 47 mmol). The mixture was heated to reflux for 10 min, then cooled to 0 °C and a solution of **71** (3.0 g, 7.1 mmol) in dry THF (30 mL) was added dropwise. The reaction mixture was refluxed overnight, cooled and poured into cold HCl (10%, 250 mL). The mixture was extracted with CH_2Cl_2 (3 x 100 mL), the organic layer was washed with water (3 x 50 mL), dried over $CaCl_2$ and evaporated. The crude product was purified through chromatography to yield **69** (2.7 g, 95%) as a pale yellow solid which was recrystallized from n-hexanes to give white crystals. M.p. 88-90°C; ^1H NMR (250 MHz) δ 8.21 (s, 2 H, Ar-H), 7.19 (s, 2 H, Ar-H), 2.57 (s, 6 H, CH_3). $^{13}C\{^1H\}$ NMR (62.9 MHz) δ 132.66, 131.58, 129.43, 127.61, 121.50, 19.10. MS (EI): *m/z* 312 [M^+ based on $(^{79}Br)_2$, 46%]; Anal. Calcd. for $C_{12}H_{10}Br_2$: C, 45.90: H, 3.21. Found: C, 46.11; H, 2.96.

2,3-Dibromo-5,8-bis(bromomethyl)naphthalene (70). Compound **69** (0.5g, 1.6mmol), NBS (0.57g, 3.2mmol), and $(PhCO)_2$ (8mg) were dissolved in CCl_4 (100ml) and refluxed for overnight. The resultig mixture was filtered and the solvent was removed. The crude product was purified through column chromatography (hexane/chlorofrom, 10:1) to give **70** as white solid (0.3g, 40%). ^1H NMR (250 MHz) δ 8.46 (s, 2H, Ar-H), 7.50 (s, 2H, Ar-H), 4.83 (s, 4H, $-CH_2Br$); $^{13}C\{^1H\}$ NMR (62.9 MHz, DMSO-d_6) δ 135.48, 131.72, 130.46, 129.94, 123.18, 32.55. MS (EI): *m/z* 468

[M^+ based on $(^{79}Br)_4$, 1.3%]; Anal. Calcd. for $C_{12}H_8Br_4$: C, 30.55; H, 1.71. Found: C, 30.81; H, 1.57.

2,3-Dibromo-5,8-dihexyloxymethylnaphthalene (71). Sodium metal (0.2 g, 8.9 mmol) was added into 1-hexanol (20 mL) in a schlenk (150 mL) under nitrogen. The solution was heated gently until all the sodium had dissolved. Compound **70** (0.84 g, 1.78 mmol) was then added to the cooled solution and the mixture was heated to reflux for 18 h. The excess alcohol was removed under reduced pressure and the residue was dissolved in diethyl ether (150 mL). The organic layer was washed with NaOH (5% aqeuous, 3 x 100 mL) and water (3 x 100 mL). The organic portion was dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by column chromatography with hexanes / ethyl acetate (15 : 1) as eluent to give **71** as a colourless liquid (0.66 g, 72%). ^1H NMR (250 MHz) δ 8.45 (s, 2 H, ArH), 7.44 (s, 2 H, ArH), 4.84 (s, 4 H, $ArCH_2$), 3.47-3.57 (pentet, J = 6.4 Hz, 4 H, CH_2), 1.59-1.63 (m, 4 H, CH_2), 1.27-1.36 (m, 14 H, CH_2), 0.84-0.89 (t, J = 6.7 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ (75.5 MHz) δ 133.8, 132.0, 129.5, 126.9, 122.5, 71.1, 70.7, 31.6, 29.7, 22.6, 14.0; MS (EI): an isotopic cluster peaking at *m/z* 512 [M^+ based on $(^{79}Br)_2$, 20%].

2,3-Dicyano-5,8-dihexyloxymethylnaphthalene (74). Compound **71** (1.0 g, 1.9 mml) and CuCN (0.5 g, 5.8 mmol) were dissolved in DMF (30 mL) and the mixture was heated at 150°C for 10 h under nitrogen. An 35% ammonia solution (40 mL) was added to the cooled mixture to which air was bubbled for 12 h. The precipitate was filtered off and washed with $CHCl_3$ (3 x 30 mL) while the filtrate was extracted with $CHCl_3$ (3 x 50 mL). The combined organic layer was washed with water (3 x 100 mL), dried over $CaCl_2$, and evaporated under vacuum. Compound **74** was obtained which was purified

by column chromatography with hexanes / ethyl acetate (7 : 1) as eluent (0.41 g, 52%). M.p. 86-88°C; ^{1}H NMR (250 MHz) δ 8.69 (s, 2 H, ArH), 7.70 (s, 2 H, ArH), 4.90 (s, 4 H, , $ArCH_2$), 3.53-3.58 (t, J = 6.6 Hz, 4 H, CH_2), 1.57-1.65 (m, 4 H, CH_2,), 1.25-1.41 (m, 12 , CH_2), 0.84-0.90 (t, J = 6.7 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ (75.5 MHz) δ 135.8, 133.2, 132.6, 130.4, 116.1, 110.1, 71.2, 70.8, 31.6, 29.6, 25.9, 22.6, 14.0; MS (EI): an isotopic cluster peaking at *m/z* 407 (M^+, 31%); I.R.: 2931s, 2857s, 2233m ($\nu_{C\equiv N}$), 1622w, 1474w, 1367w, 1090s, 890m, 856w cm^{-1}; Anal. Calcd. for $C_{26}H_{34}N_2O_2$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.20; H, 8.50; N, 6.74.

(2,5,11,14,20,23,29,32-Octahexyloxymethyl-2,3-naphthalocyaninato)zinc(II) (**79**). To a mixture of dinitrile **74** (200 mg, 0.49 mmol) and $Zn(OAc)_2 2H_2O$ (30 mg, 0.14 mmol) in 1-hexanol (10 mL) at 90°C was added DBU (0.34 mL). The mixture was refluxed under nitrogen for 20 h then poured into a mixture of methanol / acetone (1 : 1, 50 mL). The precipitate was washed with water, acetone and methanol. The crude product was purified by column chromatography with hexanes / THF (1 :1) as eluent (125 mg, 60%). ^{1}H NMR [250 MHz, C_6D_6 / C_5D_5N (v/v 3:1)] δ 10.00 (br s, 8 H, ArH), 7.92 (br s, 8 H, ArH), 5.39 (br s, 16 H, $ArCH_2$), 3.84 (br s, 16 H, OCH_2), 1.87-1.97 (m, 16 H, CH_2), 1.57-1.70 (m, 16 H, CH_2), 1.15-1.45 (m, 32 H, CH_2), 0.83 (t, J = 6.8 Hz, 24 H, CH_3); UV-Vis [THF, 4.26 x 10^{-6} M, λmax (log ε)]: 336 (5.50), 676 (5.30), 721 (5.27), 756 (6.13); MS (LSI): an isotopic cluster peaking at *m/z* 1691.07 [Calcd. for MH^+ 1691.65]; Anal. Calcd. For $C_{104}H_{136}N_8O_8Zn$: C, 73.84; H, 8.10; N, 6.62. Found: C, 72.75; H, 8.41; N, 6.37.

3.10 Preparation of [2,5,11,14,20,23,29,32-octa(2',5',8'-trioxadodecyl)-2,3-naphthalocyaninato]zinc(II) (**80**)

2,3-Dibromo-5,8-bis(2',5',8'-trioxadodecyl)naphthalene (**72**). Sodium metal (0.08 g, 3.50 mmol) was added into butyl digol (15 mL) under nitrogen. The solution was heated at 100°C to dissolve all the sodium. Compound **70** (0.66 g, 1.44 mmol) was then added to the cooled solution and the mixture was heated at 180°C for 18 h. The excess butyl digol was removed under reduced pressure and the residue was dissolved in diethyl ether (120 mL). The organic layer was washed with NaOH (5% aqeuous, 3 x 100 mL) and water (3 x 100 mL). The organic portion was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography with hexanes / ethyl acetate (4 :1) as eluent to give **72** as a colourless liquid (0.4 g, 44.2%). ^{1}H NMR (300 MHz) δ 8.48 (s, 2 H, ArH), 7.45 (s, 2 H, ArH), 4.92 (s, 4 H, $ArCH_2$), 3.58-3.69 (m, 16 H, OC_2H_4), 3.43-3.48 (t, J = 6.8 Hz, 4 H, OCH_2), 1.51-1.60 (quintet, J = 7.0 Hz, 4 H, CH_2), 1.28-1.40 (sextet, J = 7.2 Hz, 4 H, CH_2), 0.85-0.92 (t, J = 7.2 Hz, CH_3); $^{13}C\{^1H\}$ (75.5 MHz) δ 133.6, 132.0, 129.6, 127.2, 122.6, 71.5, 71.2, 70.7, 70.67, 70.1, 69.6, 31.7, 19.3, 13.9; MS (EI): *m/z* 632 [M^+ based on $(^{79}Br)_2$, 1%]; Anal. Calcd. for $C_{28}H_{42}Br_2O_6$: C, 53.01; H, 6.67. Found: C, 53.81; H, 6.99.

2,3-Dicyano-5,8-bis(2',5',8'-trioxadodecyl)naphthalene (**75**). Compound **72** (0.75 g, 1.18 mmol) and CuCN (0.34 g, 3.8 mmol) were dissolved in DMF (25 mL) and the mixture was heated at 150°C for 18 h then cooled to r.t.. An 35% Ammonia solution

(35 mL) was added to the mixture which was bubbled with air (12 h). The solid was filtered, washed with $CHCl_3$, and the filtrate was extracted with $CHCl_3$ (3 x 50 mL). The combined organic solution was washed with water (3 x 100 mL) and dried over $CaCl_2$. The solvent was removed and the crude product was purified by column chromatography with hexanes / ethyl acetate (2 :1) as eluent to give **75** as a pale green liquid (0.26 g, 42%). ^{1}H NMR (300 MHz) δ 8.76 (s, 2 H, ArH), 7.69 (s, 2 H, ArH), 4.99 (s, 4 H, $ArCH_2$), 3.60-3.72 (m, 16 H, OC_2H_4), 3.44-3.48 (t, J = 6.8 Hz, 4 H, OCH_2), 1.49-1.59 (pentet, J = 8.7 Hz, CH_2), 1.27-1.39 (sixtet, J = 7.5 Hz, CH_2), 0.86-0.90 (t, J = 7.4 Hz, CH_3); $^{13}C\{^1H\}$ NMR (75.7 MHz) δ 135.6, 133.3, 132.7, 130.6, 116.1, 110.2, 71.2, 70.8, 70.7, 70.1, 69.9, 31.7, 19.2, 13.9; MS (EI): *m/z* 528 (M^+, 4%); I.R.: 2957s, 2931s, 2868s, 2233m ($\nu_{C\equiv N}$), 1461m, 1352m, 1239w, 1104s, 1036m, 897w cm^{-1}; Anal. Calcd. for $C_{30}H_{42}N_2O_6$: C, 68.42; H, 8.04; N, 5.32. Found: C, 68.61; H, 8.16; N, 5.27.

[2,5,11,14,20,23,29,32-Octakis(2',5',8'-trioxadodecyl)-2,3-naphthalocyaninato]zinc(II) (80). To a mixture of dinitrile **75** (260 mg, 0.5 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (37 mg, 0.17 mmol) in 1-hexanol (10 mL) at 90°C was added DBU (0.35 mL). The mixture was refluxed for 20 h then the solvent was removed under reduced pressure. The crude product was purified by column chromatography with toluene / THF (1 :1) as eluent to give **80** as a deep green solid (97 mg, 36%). ^{1}H NMR [300 MHz, C_6D_6 / C_5D_5N (v/v 3 : 1)] δ 10.08 (br s, 8 H, ArH), 7.85 (br s, 8 H, ArH), 5.42 (br s, 16 H, $ArCH_2$), 4.03 (br s, 16 H, OCH_2), 3.93 (br s, 16 H, OCH_2), 3.79-3.83 (m, 16 H, OCH_2), 3.56-3.60 (m, 16 H, OCH_2), 3.29 (t, J = 6.4 Hz, 16 H, OCH_2), 1.38-1.48 (m, 16 H, CH_2), 1.24-1.34 (m, 16 H, CH_2), 0.78 (t, J = 7.3 Hz, 24 H, CH_3); $^{13}C\{^1H\}$ [75.5 MHz, C_6D_6 / C_5D_5N (v/v 3 :1)] δ 153.3, 136.2, 135.2, 131.8, 125.6, 118.7, 72.1,

71.3, 71.2, 70.8, 70.7, 70.3, 32.2, 30.1, 19.6, 14.1; I.R.: 2958s, 2928s, 2866s, 1458w, 1379w, 1344w, 1104s, 1025w, 809w cm^{-1}; Uv-Vis [THF, 4.79 x 10^{-6} M, λmax (log ε)]: 336 (5.32), 677 (5.10), 722 (5.09), 757 (5.93); MS (LSI): an isotopic cluster peaking at *m/z* 2171.57 [Calcd. for MH^+ 2172.08]; Anal. Calcd. for $C_{120}H_{168}N_8O_{24}Zn$: C, 66.36; H, 7.80; N, 5.16. Found: C, 64.71; H, 8.16; N, 4.64.

3.11 Preparation of (2,5,11,14,20,23,29,34-octadodecylthiomethyl-2,3-naphthalocyaninato)zinc(II) (**81**)

2,3-Dibromo-5,8-bis(dodecylthiomethyl)naphthalene (73). 1-dodecanethiol (1.53 mL, 6.4 mmol) was dissolved in dry DMF (80 mL) and NaOMe (0.35 g, 6.4 mmol) was added. The mixture was heated gently to dissolve all the NaOMe and then stirred for a further ½ h at r.t. under nitrogen. Compound **70** (1.01 g, 2.2 mmol) was added and the mixture was stirred at r.t. for 16 h. The white precipitate was filtered off which was purified by column chromatography with hexanes / chloroform (4 : 1) as eluent (0.85 g, 55%). ^1H NMR (300 MHz) δ 8.45 (s, 2 H, ArH), 7.30 (s, 2 H, ArH), 4.05 (s, 4 H, $ArCH_2$), 2.45 (t, J = 7.1 Hz, 4 H, SCH_2), 1.53-1.62 (m, 4 H, CH_2), 1.25-1.32 (m, 36 H, CH_2), 0.88 (t, J = 6.2 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (75.5 MHz) δ 133.2, 132.0, 129.7, 127.4, 122.5, 33.9, 32.2, 31.9, 29.6, 29.5, 29.3, 29.2, 28.9, 22.7, 14.1; MS (EI): an isotopic cluster peaking at *m/z* 712 (M^+ based on $(^{79}Br)_2$, 15%); Anal. Calcd. for $C_{36}H_{58}Br_2S_2$: C, 60.49; H, 8.18. Found: C, 60.70; H, 8.50.

2,3-Dicyano-5,8-bisdodecylthiomethylnaphthalene (76). Compound **73** (1.3 g, 1.8 mmol) and CuCN (0.49 g, 5.5 mmol) were dissolved in DMF (40 mL) and the mixture was heated at 150°C for 30 h under nitrogen. An 35% ammonia solution (40 mL) was added to the cooled mixture which was bubbled with air for 15 h. The precipitate was filtered off and washed with $CHCl_3$ (3 x 30 mL). The filtrate was extracted with $CHCl_3$ (3 x 50 mL) and the combined organic portions were washed with water (3 x 80 mL), dried over $CaCl_2$, and evaporated. The crude product was purified by column chromatography with hexanes / $CHCl_3$ (1 : 1) as eluent (0.23 g, 21%). ^1H NMR (300 MHz) δ 8.70 (s, 2 H, ArH), 7.55 (s, 2 H, ArH), 4.11 (s, 4 H, $ArCH_2$), 2.48 (t, J = 7.4 Hz, 4 H, SCH_2), (quintet, J = 7.3 Hz, 4 H, CH_2), 1.25-1.38 (m, 36 H, CH_2), 0.88 (t, J = 6.8 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (75.5 MHz) δ 135.3, 133.2, 132.6, 130.8, 116.1, 110.0, 33.8, 32.6, 31.9, 29.6, 29.5, 29.3, 29.2, 28.9, 22.7, 14.1; MS (EI): m/z at 606 (M^+, 5%); Anal. Calcd. for $C_{38}H_{58}N_2S_2$: C, 75.19; H, 9.63; N, 4.61; S, 10.56. Found: C, 75.01; H, 9.56; N, 4.71; S, 10.85.

[2,5,11,14,20,23,29,32-octa(dodecylthiomethyl)-2,3-naphthalocyaninato]-zinc(II) (81). To a mixture of dinitrile **76** (130 mg, 0.2 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (17 mg, 0.07 mmol) in 1-hexanol (10 mL) at 90°C DBU (0.15 mL) was added. The mixture was heated at 160°C for 18 h under nitrogen, cooled, and added in dropwise into a mixture of methanol / acetone (1 :1, 50 mL). The precipitate was filtered, washed with water, acetone, and methanol. The crude product was subjected to Soxhlet extraction, washed with methanol / acetone (1 : 1, 300 mL) for 2 days and then extracted out by toluene (250 mL). The solvent was evaporated to minimum and methanol was added to precipitate out compound **81** (60 mg, 45%). ^1H NMR (300 MHz) δ 10.07 (br s, 8 H,

ArH), 7.55 (br s, 8 H, ArH), 4.53 (br s, 16 H, $ArCH_2$), 2.72 (br s, 16 H, SCH_2), 1.89 (br s, 16 H, CH_2), 1.45 (br s, 16 H, CH_2), 1.20 (br s, 128 H, CH_2), 0.78-0.81 (m, 24 H, CH_3); UV-Vis [THF, 1.93 x 10^5 M, λmax (log ε)]: 340 (4.32), 683 (4.11), 728 (4.12), 765 (4.87).

3.12 Preparation of (3,4,12,13,21,22,30,31-octaoctylthio-2,3-naphthalocyaninato)zinc(II) (**82**)

2,3-Dicyano-6,7-dioctylthionaphthalene (77). 1-octanethiol (0.52 mL, 3 mmol) was added slowly into an ice-cold suspension of NaH (0.16 g, 4 mmol) in DMF (50 mL). Until the evolution of hydrogen was completed, 2,3-dibromo-6,7-dicyanonaphthlene (**11**) (0.67 g, 2.0 mmol) and Cu_2O (0.29 g, 2 mmol) were added and the mixture was refluxed for 16 h. The cooled mixture was poured into ice then extracted with Et_2O (3 x 150 mL). The combined organic portions were washed with ammonia solution (35%, 3 x 50 mL) and water (3 x 50 mL), then dried over K_2CO_3. The solvent was removed and compound **77** was obtained which was purified by column chromatography with hexanes / chloroform (1 :1) as eluent (0.45 g, 49%). ^1H NMR (300 MHz) δ 8.16 (s, 2 H, ArH), 7.58 (s, 2 H, ArH), 3.08 (t, J = 7.4 Hz, 4 H, SCH_2), 1.79 (quintet, J = 7.4 Hz, 4 H, CH_2), 1.42-1.56 (m, 4 H, CH_2), 1.28-1.31 (m, 16 H, CH_2), 0.88 (t, J = 6.6 Hz, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (300 MHz) δ 142.8, 134.1, 130.8, 123.0, 116.1, 109.3, 33.0, 31.8, 29.1, 29.0, 28.0, 22.6, 14.1; MS (EI): *m/z* at 466 (M^+, 100%); I.R.: 2952s, 2924s, 2853s,

2227m ($\nu_{C\equiv N}$), 1602w, 1571w, 1459w, 1423s, 1099m, 984w, 918m cm^{-1}; Anal. Calcd. For $C_{28}H_{40}N_2S_2$: C, 71.74; H, 8.60; N, 5.98. Found: C, 72.28; H, 8.41; N, 5.99.

(3,4,12,13,21,22,30,31-Octaoctylthio-2,3-naphthalocyaninato)zinc(II) (82). Dinitrile **77** (350 mg, 0.74 mmol) and $Zn(OAc)_2 2H_2O$ (46 mg, 0.25 mmol) were dissolved in 1-hexanol (12 mL). The mixture was heated to 90°C then DBU (0.52 mL) was added and refluxed for 12 h under nitrogen. The cooled solution was added in dropwise into a mixture of methanol / acetone (1 :1, 50 mL). The precipitate obtained was washed with water, acetone and methanol. Compound **82** was purified by column chromatography with THF as eluent to give a deep green solid (250 mg, 70%). ^1H NMR [300 MHz, C_6D_6 / C_5D_5N (v/v 3 : 1)] δ 9.47 (br s, 8 H, ArH), 8.20 (br s, 8 H, ArH), 3.22 (br s, 16 H, SCH_2), 1.97 (br s, 16 H, CH_2), 1.61 (br s, 16 H, CH_2), 1.35 (m, 64 H, CH_2), 0.93 (t, J = 6.3 Hz, 24 H, CH3); $^{13}C\{^1H\}$ NMR [75.5 MHz, C_6D_6 / C_5D_5N (v/v 3 :1)] δ 153.2, 137.5, 135.8, 132.3, 127.7, 120.8, 33.9, 32.3, 29.9, 29.8, 29.2, 23.2, 14.4; I.R.: 2957.18s, 2923s, 2852s, 1457m, 1409m, 1344m, 1103s, 1033w, 977w, 903w, 728m cm^{-1}; UV-Vis [THF, 7.87 x 10^{-8} M, λmax (log ε)]: 350 (5.62), 696 (5.31), 737 (5.36), 779 (6.03); Anal. Calcd. for $C_{112}H_{152}N_8S_8Zn$: C, 69.62; H, 7.93; N, 5.80. Found: C, 69.10; H, 8.23; N, 5.63.

3.13 Preparation of (3,4,12,13,21,22,30,31-octadodecylthio-2,3-naphthalocyaninato)zinc(II) (**83**)

2,3-Dicyano-6,7-didodecylthionaphthalene (**78**). 1-dodecanethiol (1 mL, 4.4 mmol) was added carefully to an ice-cold suspension of NaH (0.24 g, 6 mmol) in DMF (50 mL). Until the evolution of hydrogen was completed, 2,3-dibromo-6,7-dicyanonaphthalene (**11**) (0.68 g, 2 mmol) and Cu_2O (0.56 g, 4 mmol) were added, and the mixture was heated at 120°C for 16 h. Compound **78** was obtained and purified by column chromatography with hexanes / chloroform (1 :1) as eluent (0.35 g, 30 %). M.p. 107-108°C; ^{1}H NMR (300 MHz) δ 8.16 (s, 2 H, ArH), 7.58 (s, 2 H, ArH), 3.09 (t, J = 7.3 Hz, 4 H, $ArCH_2$), 1.26 (m, 12 H, CH_2), 0.85-0.90 (t, J = 6.6 Hz, 3 H, CH3); ^{13}C{^{1}H} (75.5 MHz) δ 142.8, 134.1, 130.8, 123.0, 116.1, 109.2, 33.0, 31.9, 29.6, 29.5, 29.3, 29.2, 29.0, 28.0, 22.7, 14.1; MS (EI): *m/z* at 578 (M^+, 14%); I.R.: 2956m, 2919s, 2849s, 2220w ($\nu_{C\equiv N}$), 1468w, 1105w, 910w cm^{-1}; Anal. Calcd. for $C_{36}H_{54}N_2S2$: C, 74.68; H, 9.40; N, 4.84. Found: C, 74.29; H, 9.61; N, 4.74.

(3,4,12,13,21,22,30,31-Octadodecylthio-2,3-naphthalocyaninato)zinc(II) (**83**). Compound **78** (230 mg, 0.4 mmol) and $Zn(OAc)_2 2H_2O$ (24 mg, 0.13 mmol) in 1-hexanol (10 mL) at 90°C was added DBU (0.35 mL) and the mixture was heated at 150°C for 12 h under nitrogen. The cooled solution was then added in dropwise into methanol /acetone (1 :1, 50 mL). The precipitate collected was washed with water, acetone, and methanol. Compound **83** was purified by column chromatography with THF as eluent to give a deep green solid (100 mg, 42%). ^{1}H NMR [300 MHz, C_6D_6

/C_5D_5N (v/v 3 :1)] δ 9.53 (br s, 8 H, ArH), 8.27 (br s, 8 H, ArH), 3.29 (br s, 16 H, SCH_2), 2.05 (br s, 16 H, CH_2), 1.70 (br s, 16 H, CH_2), 1.20-1.60 (m, 128 H, CH_2), 0.90 (t, J = 6.7 Hz, 24 H, CH_3); $^{13}C\{^1H\}$ NMR [75.5 MHz, C_6D_6 /C_5D_5N (v/v 3 :1)] δ 153.3, 137.6, 135.8, 132.4, 127.3, 120.9, 34.0, 32.4, 30.3, 30.3, 30.0, 29.3, 23.2, 14.4; UV-Vis [THF, 1.85 x 10^{-7} M, λmax (log ε)]:347 (5.49), 697 (5.13), 743 (5.16), 780 (5.92); I.R.: 2920s, 2850s, 1412m, 1345m, 1100m cm^{-1}; Anal. Calcd. for $C_{144}H_{216}N_8S_8Zn$: C, 72.63; H, 9.14; N, 4.71. Found: C, 70.51; H, 9.40; N, 4.66.

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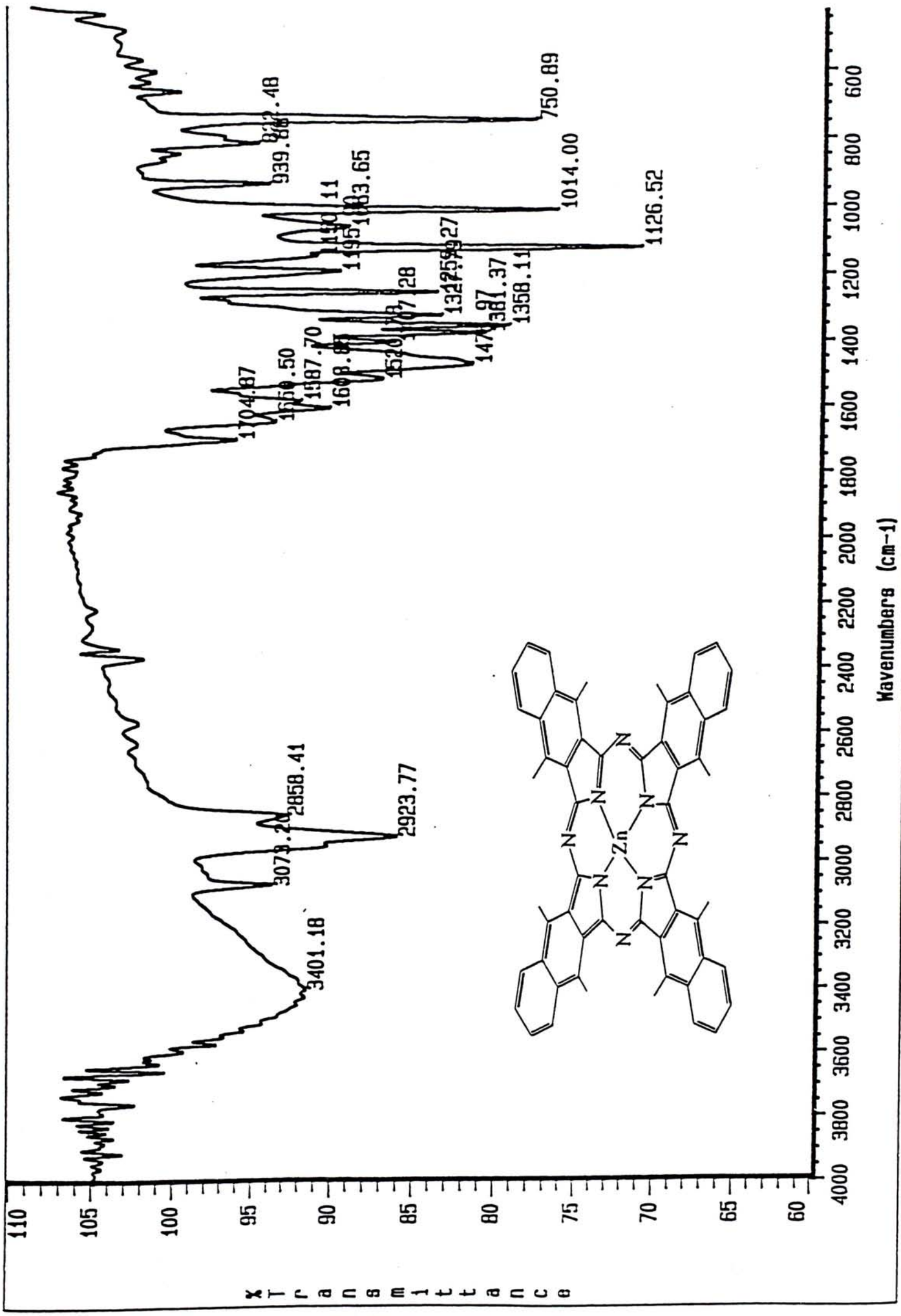
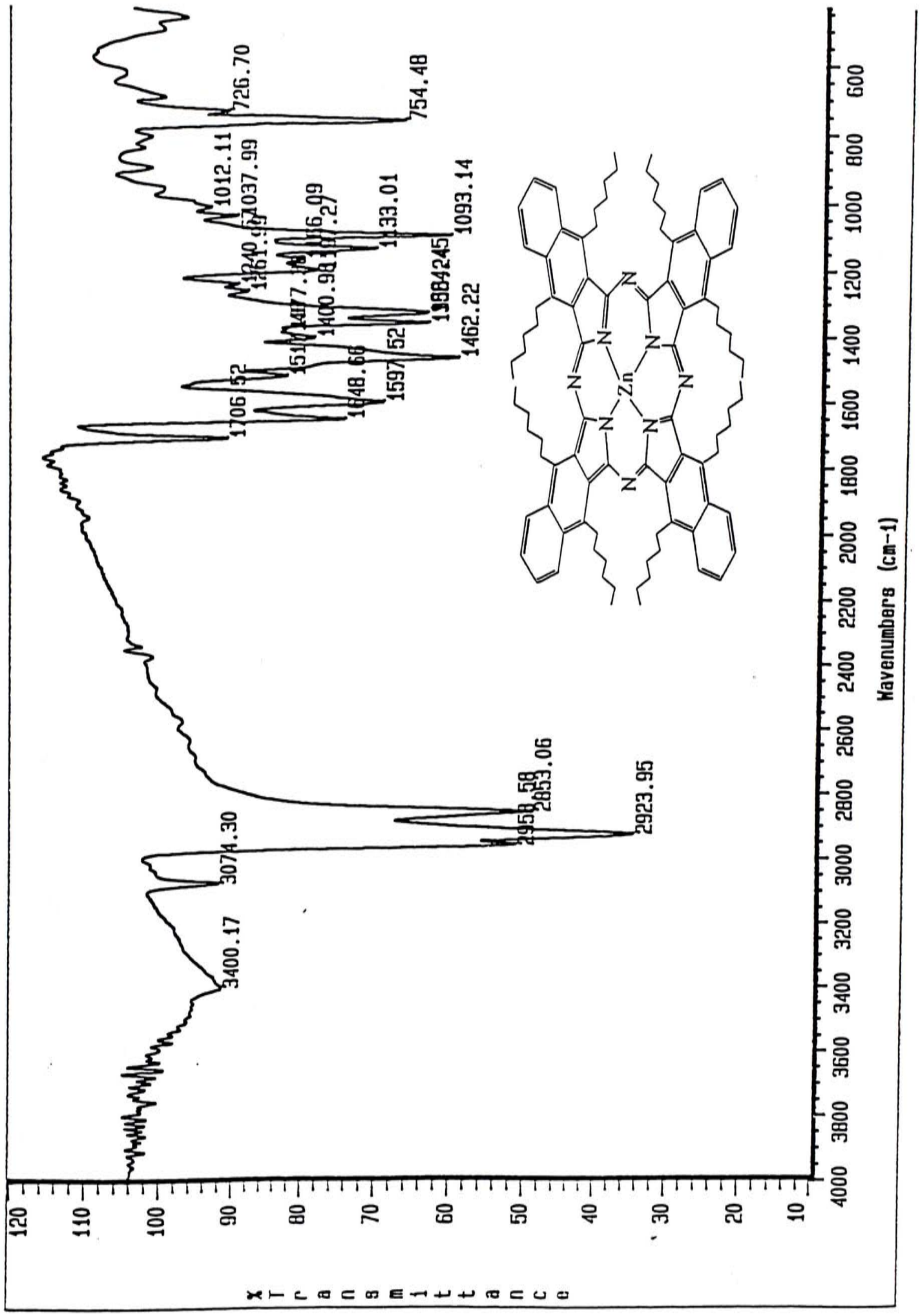
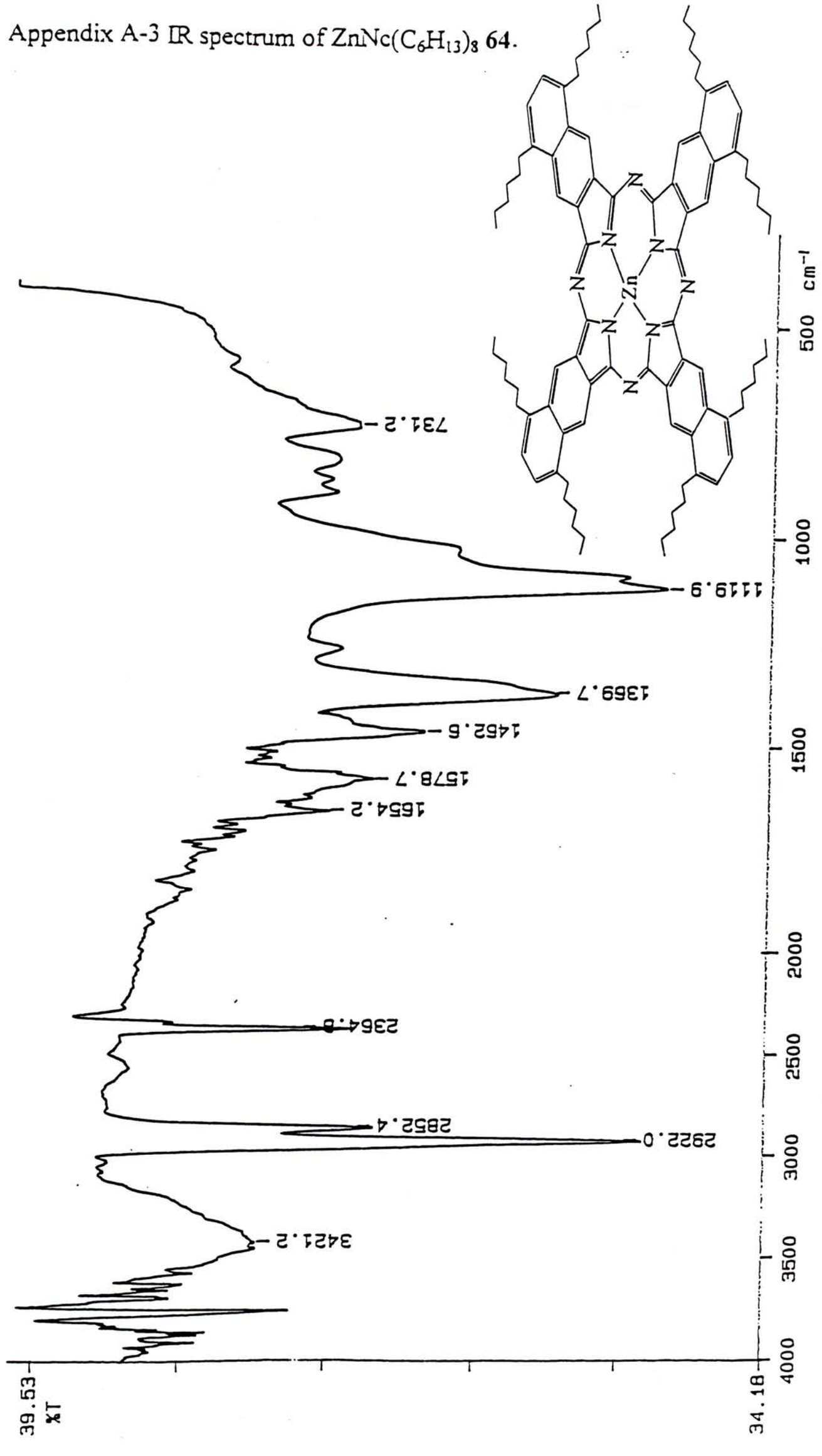
Appendix A-1 IR spectrum of $ZnNc(CH_3)_8$ **62**.



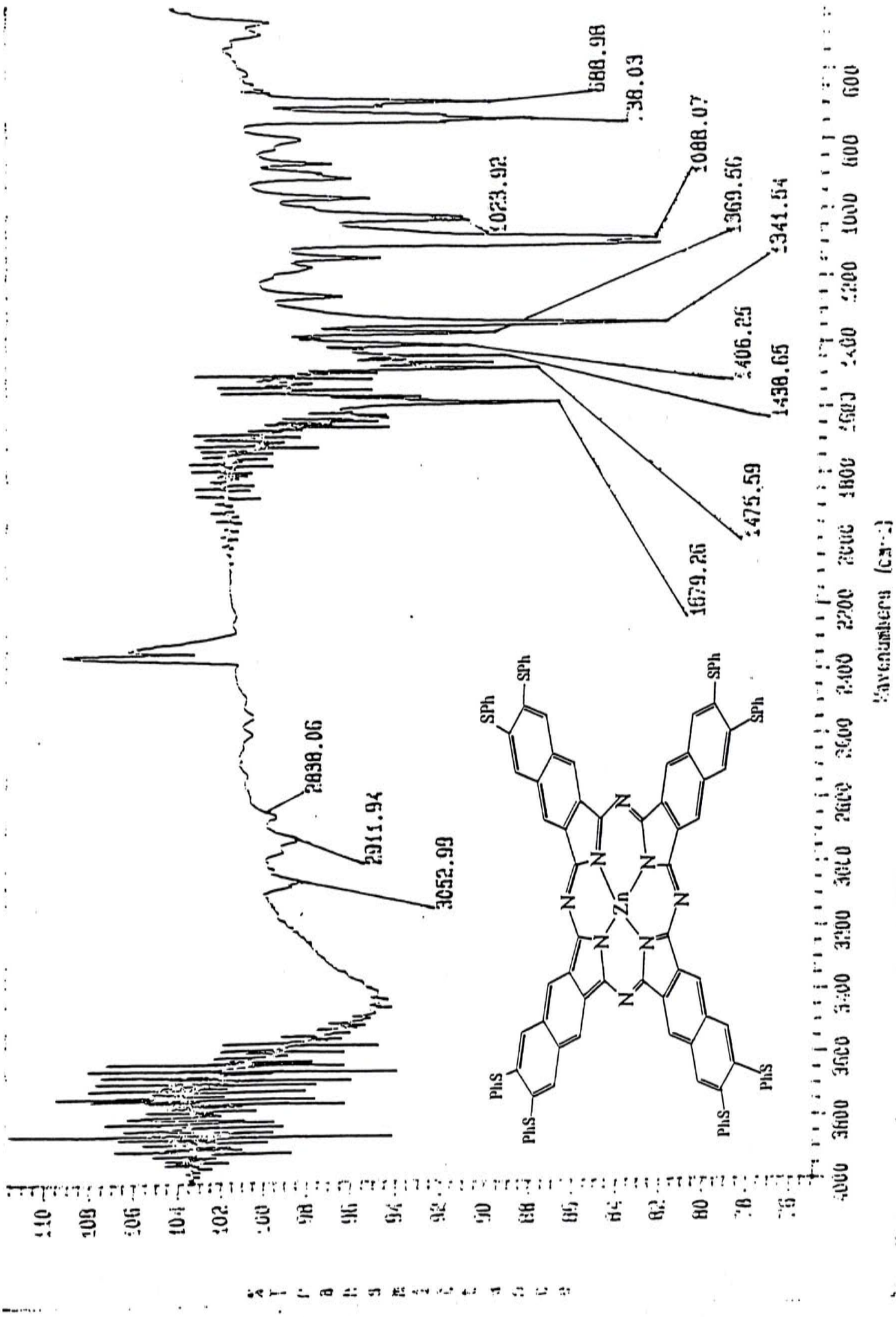
Appendix A-2 IR spectrum of $ZnNc(C_6H_{13})_8$ **63**.



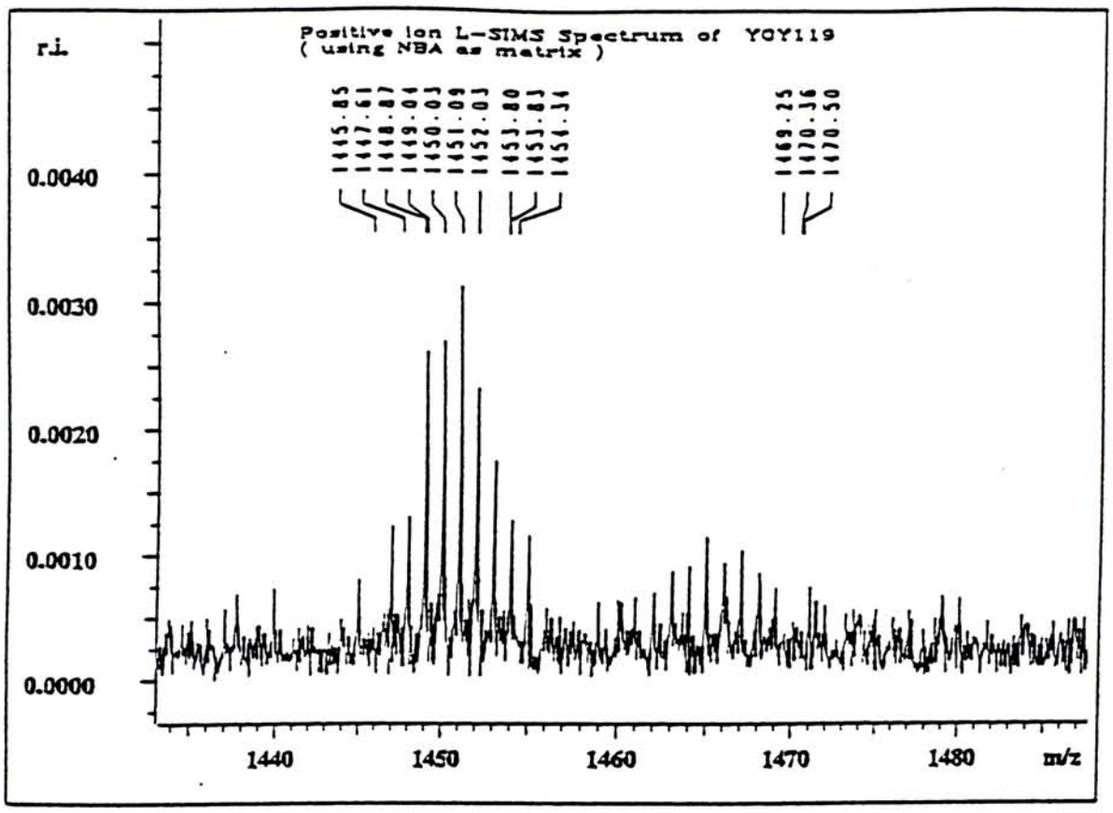
Appendix A-3 IR spectrum of $ZnNc(C_6H_{13})_8$ **64**.

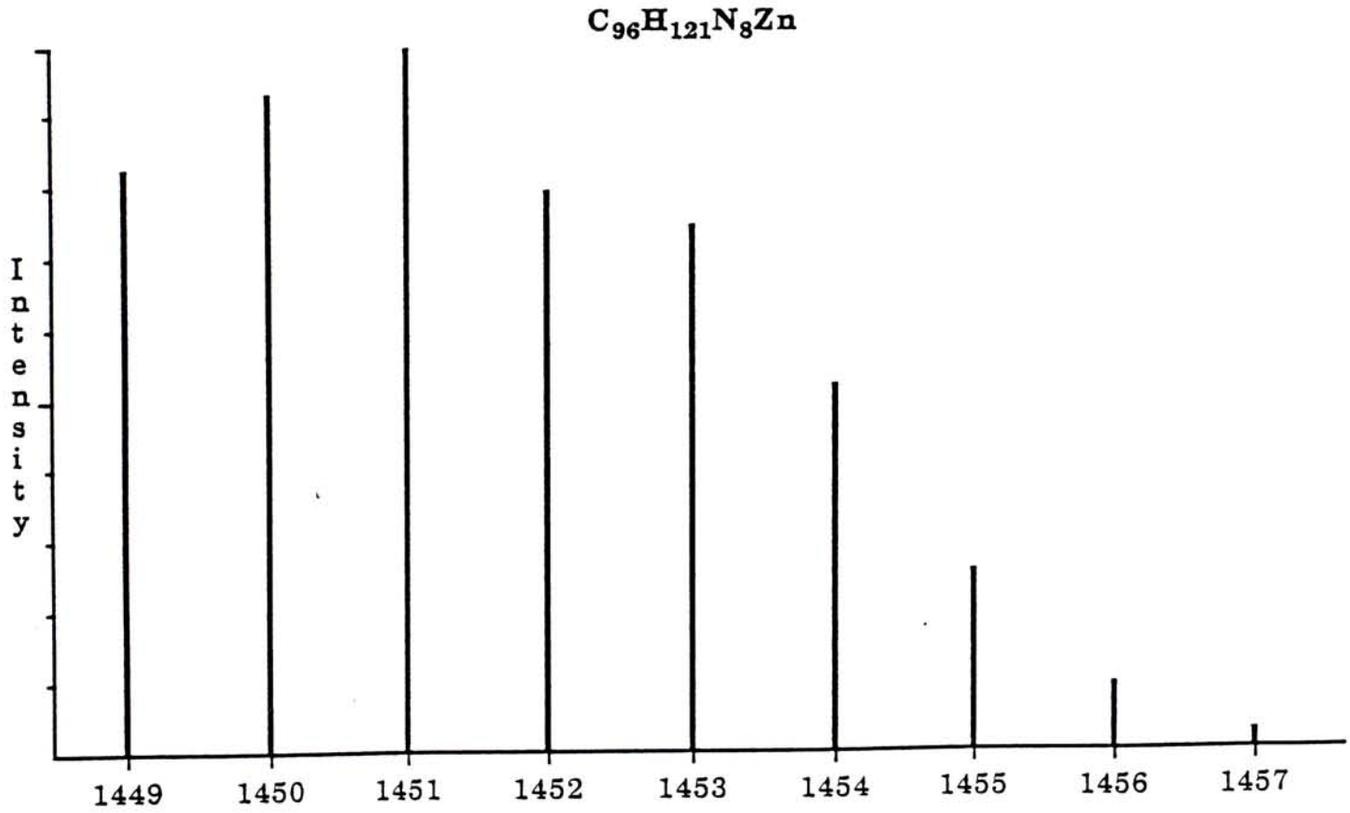


Appendix A-4 IR spectrum of $ZnNc(SPh)_8$ **66**.

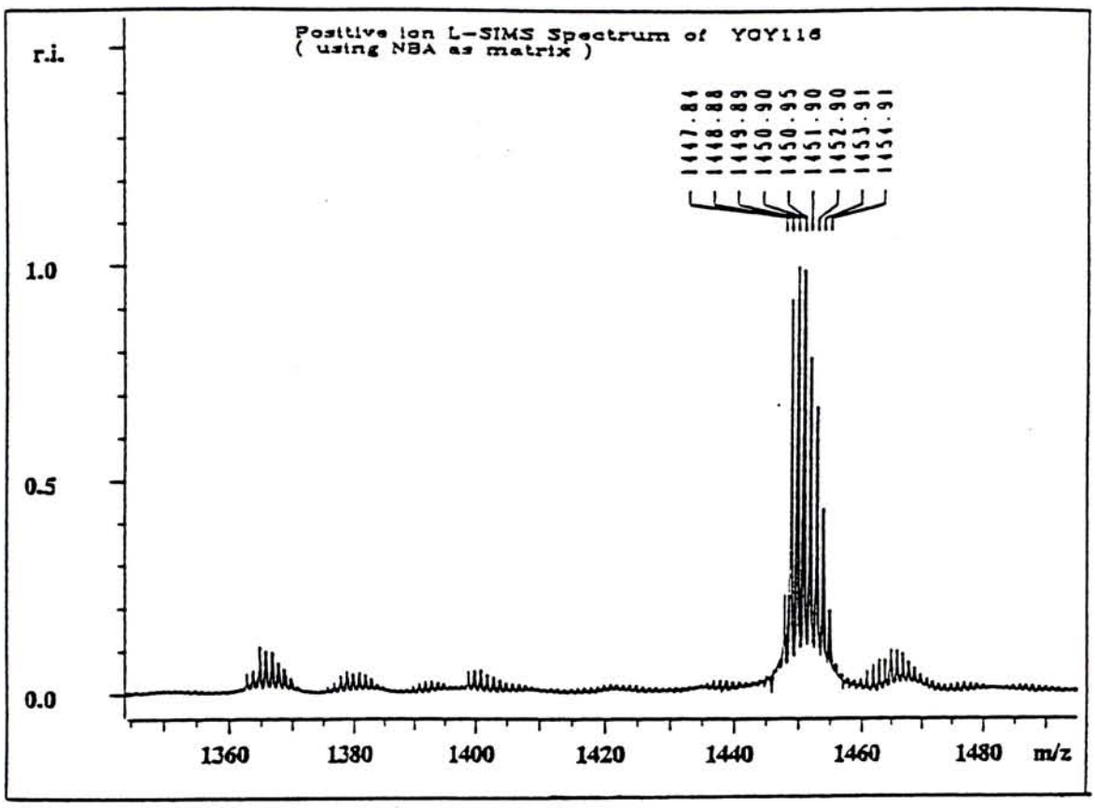


Appendix B-1 The LSI mass spectrum of **63** showing the isotopic distribution of MH^+ with the corresponding simulated pattern.

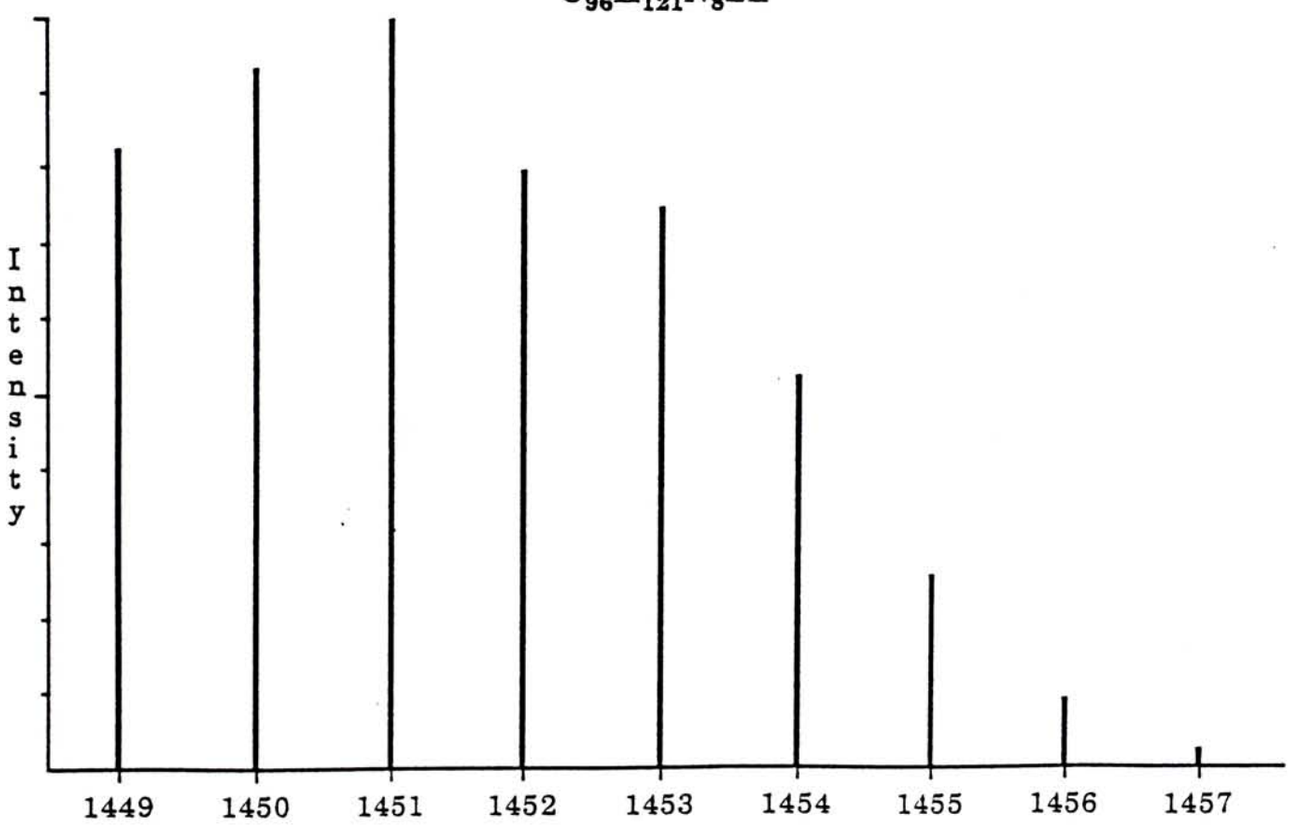




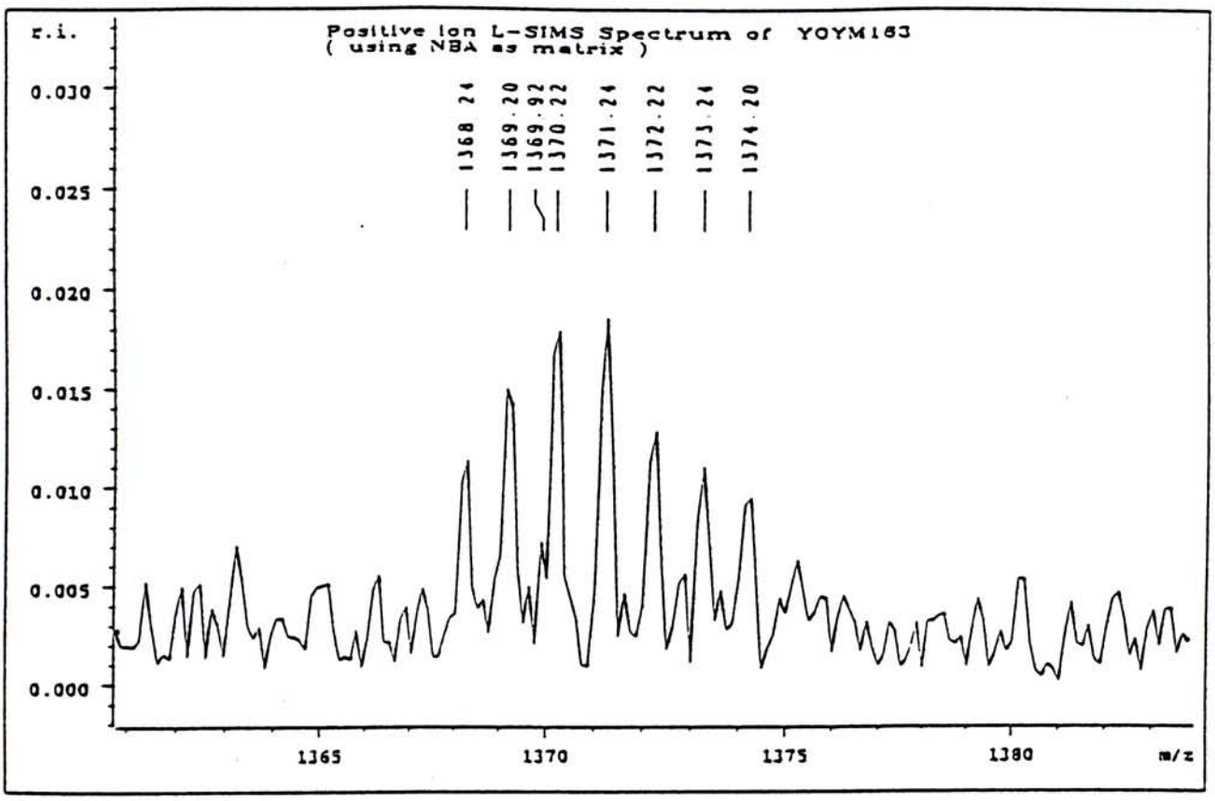
Appendix B-2 The LSI mass spectrum of **64** showing the isotopic distribution of MH^+ with the corresponding simulated pattern.

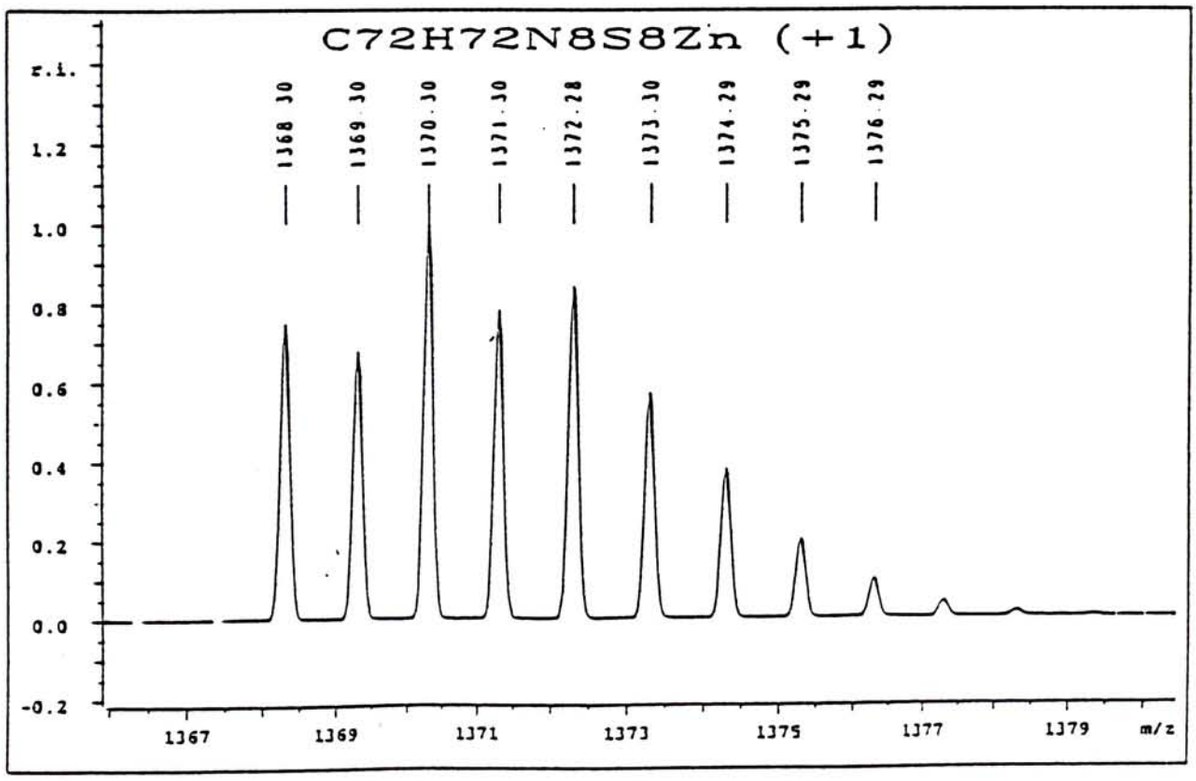


$C_{96}H_{121}N_8Zn$

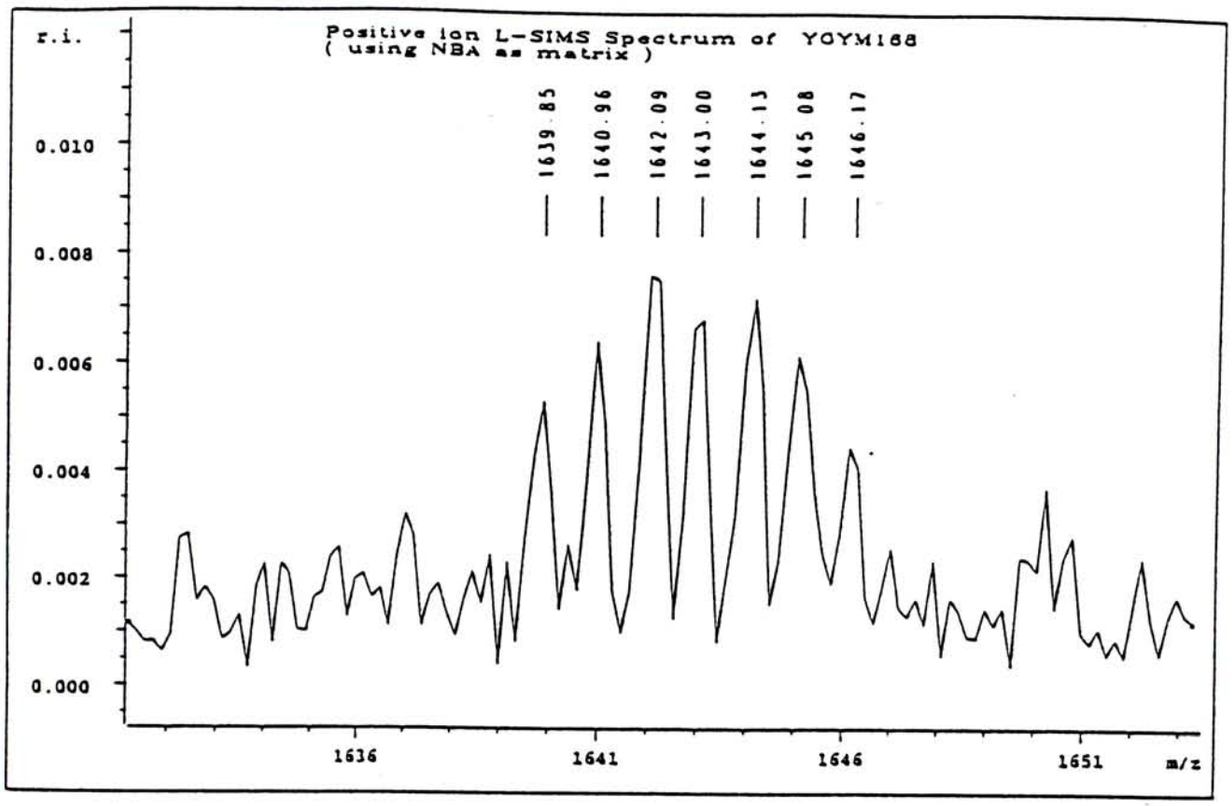


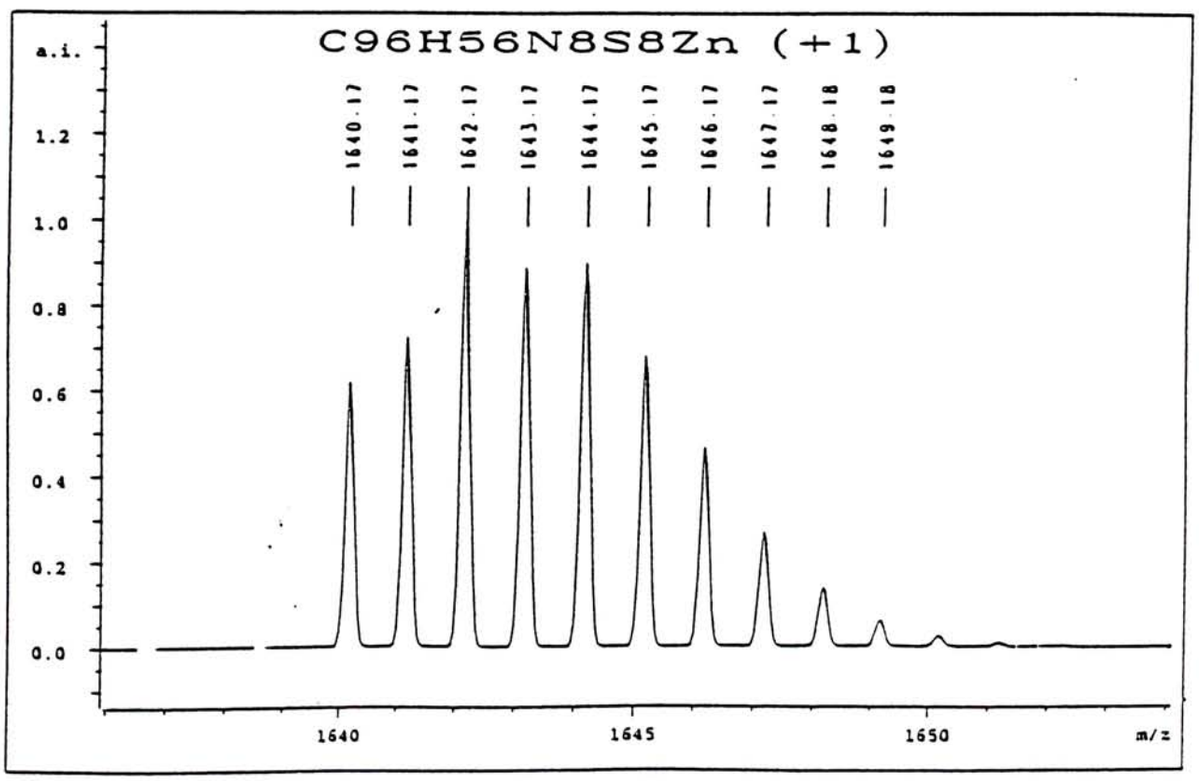
Appendix B-3 The LSI mass spectrum of **65** showing the isotopic distribution of MH^+ with the corresponding simulated pattern.





Appendix B-4 The LSI mass spectrum of **66** showing the isotopic distribution of MH^+ with the corresponding simulated pattern.





Appendix C Determination of aggregation number (n) and aggregation constant (K)[†]

Assuming a one-step equilibrium between 2,3-naphthalocyanine monomer (Nc) and aggregated 2,3-naphthalocyanine (Nc_n), the equilibrium by eq.1 is established, where K is the aggregation constant and n is the aggregation number.

$$n\,Nc \overset{K}{\rightleftharpoons} Nc_n \qquad (1)$$

K is given by eq. 2, where (1-x) is the fraction of monomer concentration to the total concentration of 2,3-naphthalocyanine, C_t.

$$K = x/[n \cdot C_t^{n-1} \cdot (1-x)^n] \qquad (2)$$

Observed extinction coefficient (ε) at certain wavelength (λ) is represented by eq. 3, where ε_m and ε_n are extinction coefficients for pure monomer and aggregate at λ, respectively.

$$\varepsilon = x \cdot\cdot \varepsilon_n/n + (1-x) \cdot \varepsilon_m \qquad (3)$$

From (2) and (3), eq. 4 is obtained.

$$\mathrm{Log}[C_t(1-\varepsilon/\varepsilon_m)] = \log(C \cdot K) + n \cdot \log\{C_t[\varepsilon/\varepsilon_m - \varepsilon_n/(n-\varepsilon_m)]\}, \qquad (4)$$

where $C = n^n/(n-\varepsilon_n/\varepsilon_m)^{n-1}$

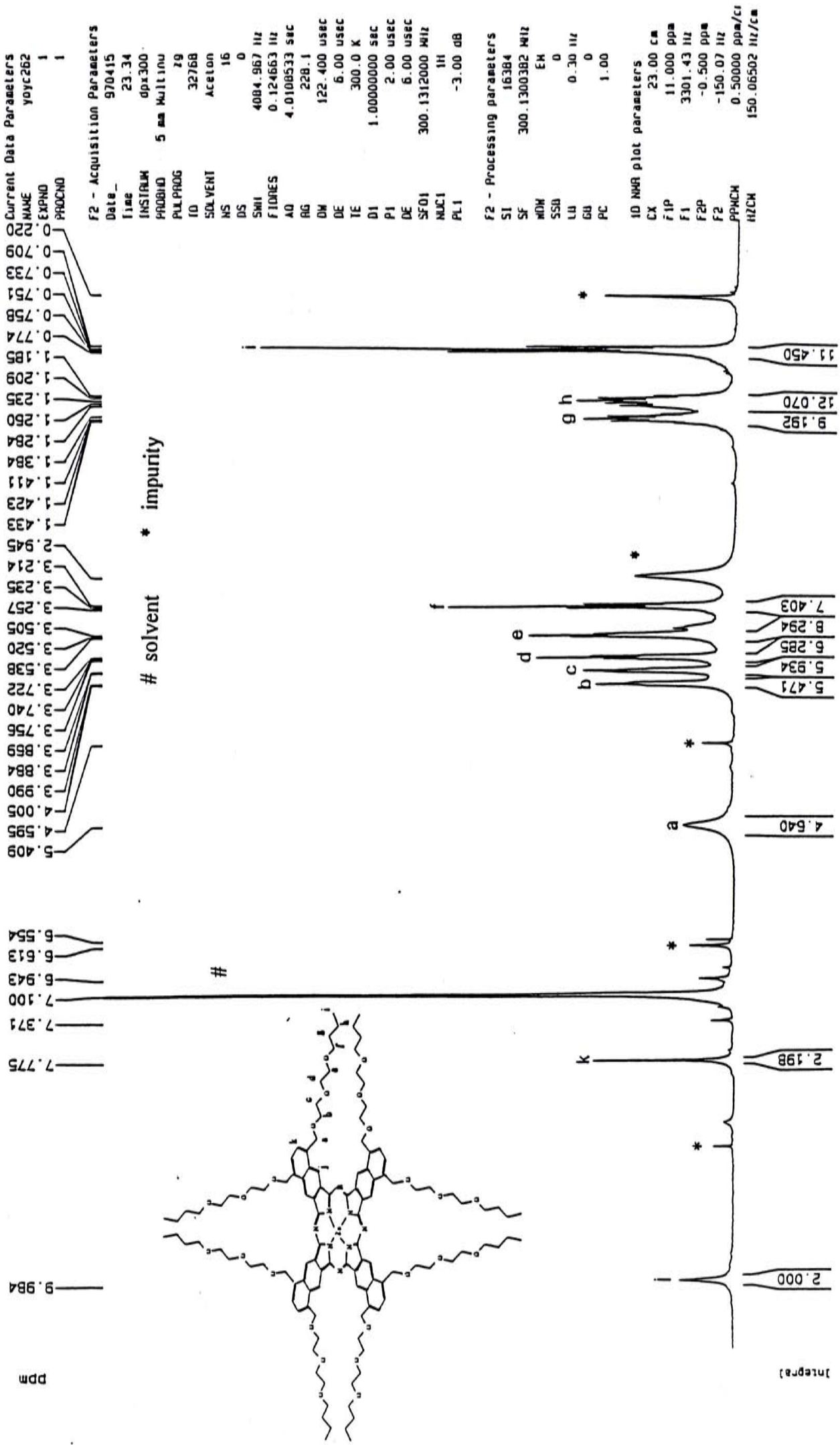
If the extinction of n-aggregate, ε_n, is very small relative to ε_m at the absorption maximum of the monomer, (4) is simplified to eq. 5 at the absorption maximum by assuming $\varepsilon/\varepsilon_m >> \varepsilon_n/(n \cdot \varepsilon_m)$ and $n >> \varepsilon_n/\varepsilon_m$.

$$\mathrm{Log}[C_t(1-\varepsilon/\varepsilon_m)] + \log(n \cdot K) + n \cdot \log[C_t(\varepsilon/\varepsilon_m)] \qquad (5)$$

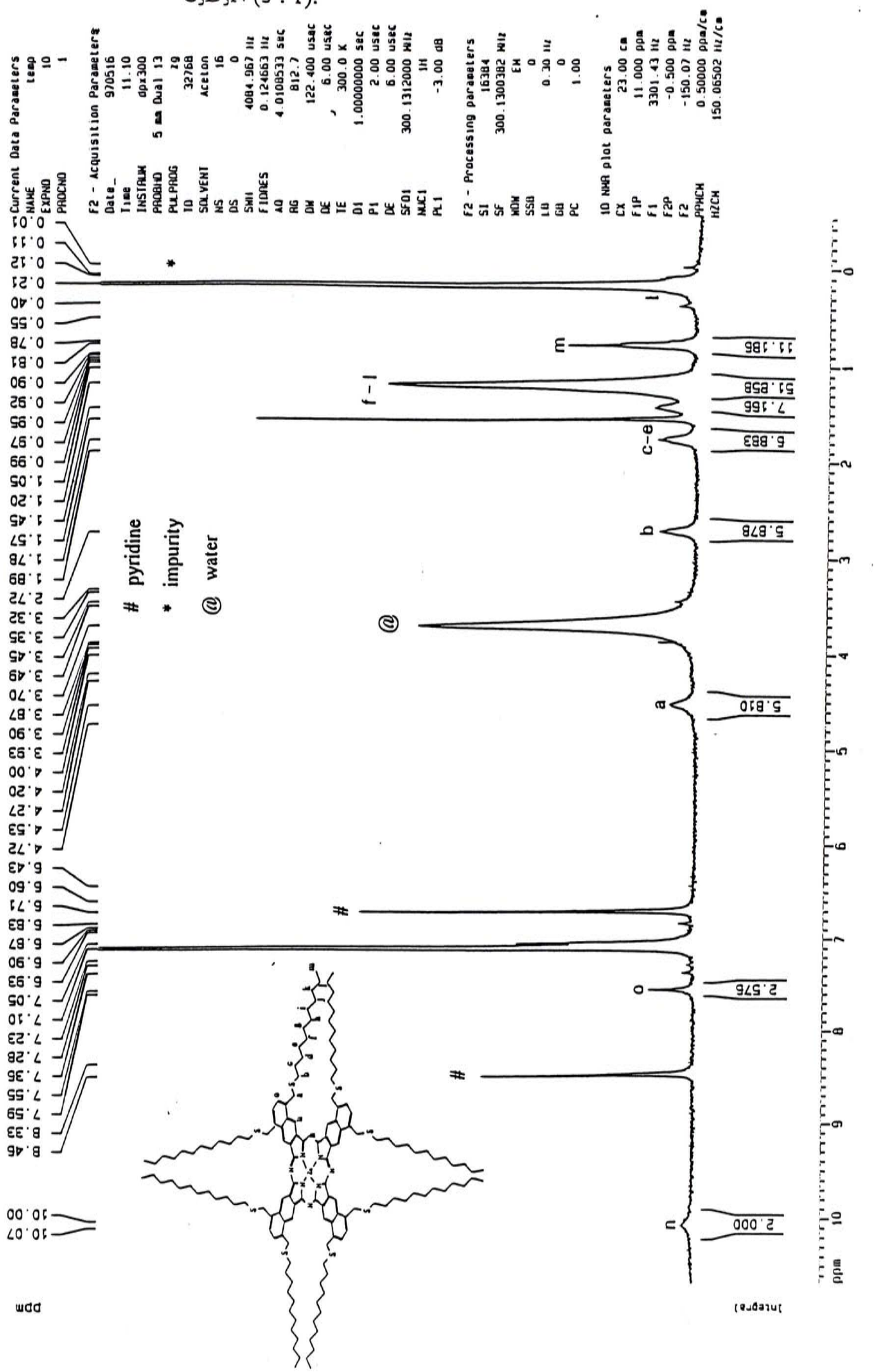
Plot of $\log[C_t(1-\varepsilon/\varepsilon_m)]$ vs. $\mathrm{Log}[C_t(\varepsilon/\varepsilon_m)]$ will give a straight line. The slope of the line represent the aggregation number (n). From the intercept [$\log(n \cdot K)$] and the n-value, the aggregation constant (K) is obtained.[†]

[†] Tai, S.; Hayashi, N. *J. Chem. Soc., Perkin Trans 2.* **1991**, 1275.
Mataga, N. *Bull. Chem. Soc. Jpn.* **1957**, *30*, 375.

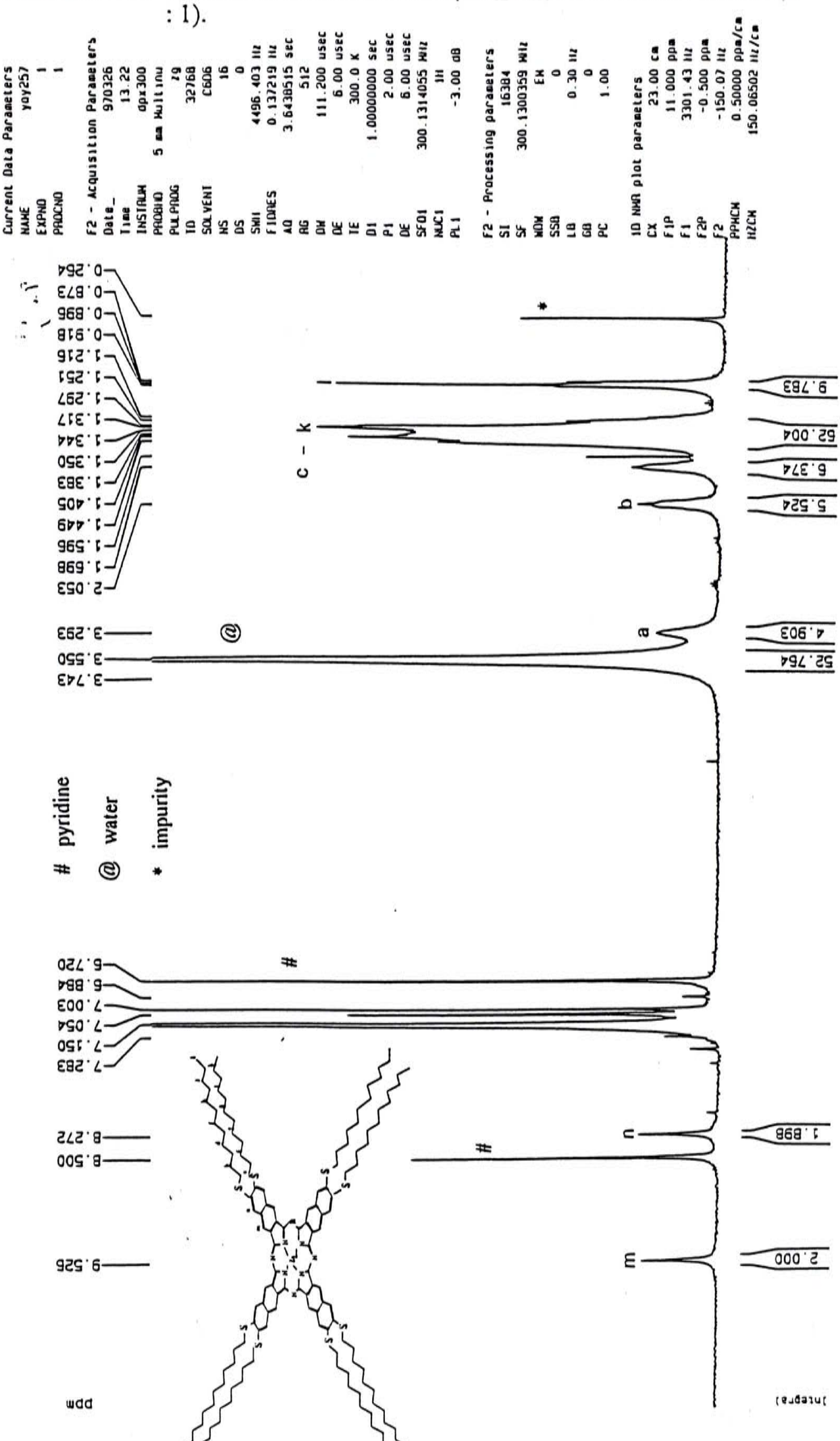
Appendix D-1 ^{1}H NMR spectrum of $ZnNc[CH_2(C_2H_4O)_2C_4H_9]_8$ **80** in C_6D_6 / C_5D_5N (3 : 1).



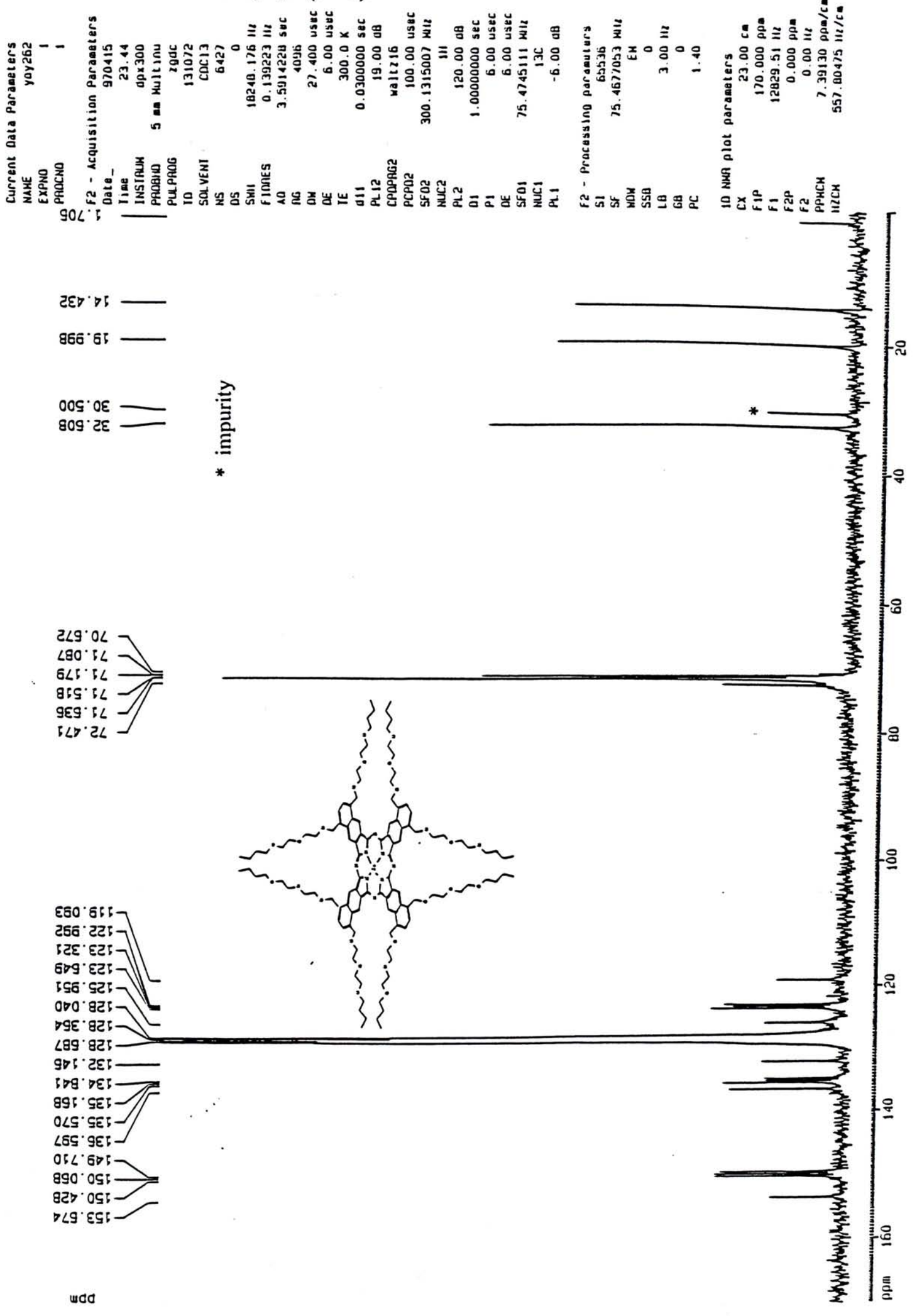
Appendix D-2 ^{1}H NMR spectrum of ZnNc[$CH_2(SC_{12}H_{25})]_8$ **81** in C_6D_6 / C_5D_5N (3 : 1).



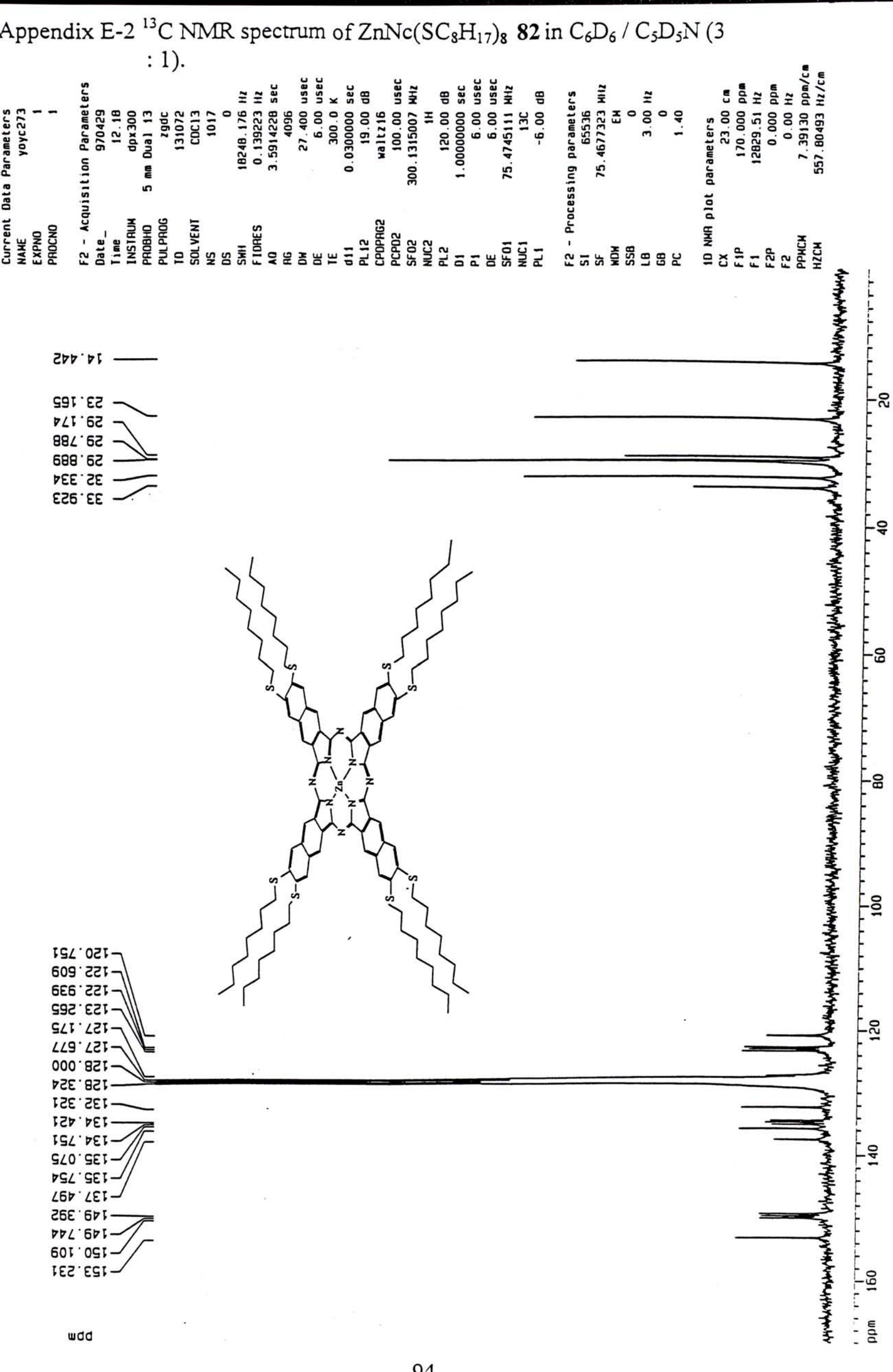
Appendix D-3 ^{1}H NMR spectrum of $ZnNc(SC_{12}H_{25})_8$ **83** in C_6D_6 / C_5D_5N (3 : 1).



Appendix E-1 ^{13}C NMR spectrum of $ZnNc[CH_2(C_2H_4O)_2C_4H_9]_8$ **80** in C_6D_6 / C_5D_5N (3 : 1).



Appendix E-2 ^{13}C NMR spectrum of $ZnNc(SC_8H_{17})_8$ **82** in C_6D_6 / C_5D_5N (3 : 1).



Appendix E-3 ^{13}C NMR spectrum of $ZnNc(SC_{12}H_{25})_8$ **83** in C_6D_6 / C_5D_5N (3 : 1).